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14. ABSTRACT Eight binary salts that pair triazolium(1+), imidazolium(1+), pyrimidinium(1+), or puri-nium(1+) cations with the icosahedral <i>closo</i> -dodecafluorododecaborate(2–) anion (B <sub>12</sub> F <sub>12</sub> <sup>2–</sup> ) were synthesized using open-air benchtop metathesis reactions in water or acetonitrile. The scale of the reactions varied from just milligrams to nearly one gram of the starting material K <sub>2</sub> B <sub>12</sub> F <sub>12</sub> . Other reaction conditions, the scope of the reaction, and the solubilities for the new salts are discussed. Five of the [heterocyclium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] salts, which were obtained in yields ranging from 84% to 99%, displayed significantly higher densities than the corresponding previously-reported analogous [heterocyclium] <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ] and [heterocyclium][CB <sub>11</sub> H <sub>12</sub> ] salts. A ninth high-density salt consisted of B <sub>12</sub> F <sub>12</sub> <sup>2–</sup> paired with an Ag <sub>4</sub> (triazole) <sub>8</sub> <sup>4+</sup> cation. The structures of eight of the nine new compounds were determined by single-crystal X-ray diffraction analysis. The density of five [heterocyclium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] salts was found to increase approximately linearly as the distance between the five-membered-ring heterocyclium(1+) cation centroids decreased. This work demonstrates additional flexibility for the rational design of ionic structures with predictable properties, which will ultimately permit the tailoring of ingredient-response behavior.					
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**Pairing heterocyclic cations with *closo*-dodecafluorododecaborate(2<sup>−</sup>).**  
**Synthesis of binary heterocyclium(1<sup>+</sup>) salts and**  
**a Ag<sub>4</sub>(heterocycle)<sub>8</sub><sup>4+</sup> salt of B<sub>12</sub>F<sub>12</sub><sup>2−</sup>**

John L. Belletire<sup>a</sup>, Stefan Schneider<sup>b</sup>, Scott A. Shackelford<sup>b\*</sup>,  
Dmitry V. Peryshkov,<sup>c</sup> Steven H. Strauss<sup>c\*\*</sup>

<sup>a</sup> *ERC, Inc., AFRL/RZSP, 10 East Saturn Blvd., Edwards AFB, 93524-7680*

<sup>b</sup> *Air Force Research Laboratory, AFRL/RZSP, 10 East Saturn Blvd., Edwards AFB, CA 92524-7680*

<sup>c</sup> *Department of Chemistry, Colorado State University, Ft. Collins, CO 80523*

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**Abstract**

Eight binary salts that pair triazolium(1<sup>+</sup>), imidazolium(1<sup>+</sup>), pyrimidinium(1<sup>+</sup>), or purinium(1<sup>+</sup>) cations with the icosahedral *closo*-dodecafluorododecaborate(2<sup>−</sup>) anion (B<sub>12</sub>F<sub>12</sub><sup>2−</sup>) were synthesized using open-air benchtop metathesis reactions in water or acetonitrile. The scale of the reactions varied from just milligrams to nearly one gram of the starting material K<sub>2</sub>B<sub>12</sub>F<sub>12</sub>. Other reaction conditions, the scope of the reaction, and the solubilities for the new salts are discussed. Five of the [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts, which were obtained in yields ranging from 84% to 99%, displayed significantly higher densities than the corresponding previously-reported analogous [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] and [heterocyclium][CB<sub>11</sub>H<sub>12</sub>] salts. A ninth high-density salt consisted of B<sub>12</sub>F<sub>12</sub><sup>2−</sup> paired with an Ag<sub>4</sub>(triazole)<sub>8</sub><sup>4+</sup> cation. The structures of eight of the nine new compounds were determined by single-crystal X-ray diffraction analysis. The density of five [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts was found to increase approximately linearly as the distance between the five-membered-ring heterocyclium(1<sup>+</sup>) cation centroids decreased. This work demonstrates additional flexibility for the rational design of ionic structures with predictable properties, which will ultimately permit the tailoring of ingredient-response behavior.

*Keywords:* heterocyclium; dodecafluorododecaborate; perfluoroborane; icosahedral borane; icosahedral carborane; metathesis

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\*Corresponding Author. Tel. +1 661 718 2665; fax arranged by e-mail or telecom  
E-mail: scott.shack@roadrunner.com (S. A. Shackelford).

\*\*Corresponding Author. Tel +1 970 491 5104; fax +1 970 491 1801  
E-mail: steven.strauss@colostate.edu (S. H. Strauss).

## 1. Introduction

Eight new binary salts that pair the icosahedral *closo*-dodecafluorododecaborate(2−) anion ( $\text{B}_{12}\text{F}_{12}^{2-}$ ) with heterocyclium(1+) cations and one new salt of  $\text{B}_{12}\text{F}_{12}^{2-}$  with a tetrameric  $\text{Ag}_4(\text{triazole})_6^{4+}$  cation were synthesized and characterized. All nine salts were prepared using open-air metathesis reactions in which stoichiometric amounts of a heterocyclium(1+) halide and  $\text{K}_2\text{B}_{12}\text{F}_{12}$  were mixed in either water or acetonitrile.

The  $\text{B}_{12}\text{F}_{12}^{2-}$  dianion is analogous to the isostructural  $\text{B}_{12}\text{H}_{12}^{2-}$  anion that was first reported by Pitochelli and Hawthorne in 1960 [1]. The  $\text{B}_{12}\text{H}_{12}^{2-}$  anion has been called a "super-aromatic" polyhedral-shaped structure, with 26 delocalized valence electrons in its  $\sigma$ -bonded framework, and is conceptually similar to the delocalized  $\pi$ -systems of planar aromatic hydrocarbons such as benzene [2–4]. The clustering of 12 B atoms into an icosahedral cage provides a polycenter of delocalized boron orbital bonding, which, like aromatic hydrocarbon rings, is very stable to chemical attack [5]. The 12 B–H vertexes of  $\text{B}_{12}\text{H}_{12}^{2-}$ , like the C–H vertexes in benzene, can undergo a wide variety of aromatic substitution reactions [2–4]. This characteristic permitted the synthesis of the  $\text{B}_{12}\text{F}_{12}^{2-}$  dianion by electrophilic attack of supercritical HF in 1992 (it was isolated as  $\text{Cs}_2(\text{H}_2\text{O})\text{B}_{12}\text{F}_{12}$  in 38% yield) [6]. Since then, the structures of nine other salts of  $\text{B}_{12}\text{F}_{12}^{2-}$  have been reported. The first of the nine was the structure of  $[\text{CPh}_3]_2[\text{B}_{12}\text{F}_{12}]$  (also reported was an improved synthesis of  $\text{K}_2\text{B}_{12}\text{F}_{12}$  in 72% yield) [7]. The next three were salts contained bridged heterocyclium(2+) cations, where the functional unsaturated sites, centered in the alkyl-based bridge structure, have heterocyclium(1+) moieties tethered at each alkyl bridge terminus [8]. More recent examples include a detailed X-ray crystal structure of  $\text{K}_2\text{B}_{12}\text{F}_{12}$  [9], the reactant used in the metathesis reactions described herein, and in the synthesis of the heterocyclium(2+) salts [8]. Finally, the structures of  $\text{K}_2(\text{H}_2\text{O})_2\text{B}_{12}\text{F}_{12}$  [10],  $\text{K}_2(\text{H}_2\text{O})_2\text{B}_{12}\text{F}_{12}$  [10],  $\text{K}_3(\text{AsF}_6)\text{B}_{12}\text{F}_{12}$  [11], and  $\text{Cs}_3(\text{AsF}_6)\text{B}_{12}\text{F}_{12}$  [11] have just been reported (the latter two are rare examples of salts containing fluoroanions with different shapes and charges).

The binary  $[\text{heterocyclium}]_2[\text{B}_{12}\text{F}_{12}]$  salts containing two heterocyclium(1+) cations reported in this work represent a new type of  $\text{B}_{12}\text{F}_{12}^{2-}$  salt. These salts, and all previously

reported [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] [12,13] and [heterocyclium][CB<sub>11</sub>H<sub>12</sub>] salts [12–16], have a unique common characteristic. For each type, a planar aromatic  $\pi$ -electron-delocalized heterocyclium(1+) cation is stoichiometrically paired with a polyhedral (icosahedral or pseudo-icosahedral) aromatic  $\sigma$ -electron-delocalized dianion in the same lattice [12,13]. Examples of each of the three types of salt we have studied are shown in Fig. 1.

The previously reported binary heterocyclium(1+) salts containing B<sub>12</sub>H<sub>12</sub><sup>2-</sup> and CB<sub>11</sub>H<sub>12</sub><sup>-</sup> can be divided into two general types based on their solubilities. Some are only sparingly soluble in H<sub>2</sub>O and precipitated from the aqueous metathesis-reaction medium during the open-air benchtop synthesis [12]. Others were very soluble in H<sub>2</sub>O and could be isolated in pure form only by repeated extraction of the crude solid reaction product with hot CH<sub>3</sub>CN, followed by subsequent removal of the solvent [13].

The new [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts, which are shown in Fig. 2, were of the same two types: some were essentially insoluble in H<sub>2</sub>O and others were quite soluble. Therefore, they were isolated and purified by procedures parallel to those discussed above. Salts **2**, **5**, and **6** could be synthesized using either H<sub>2</sub>O or CH<sub>3</sub>CN as the solvent.

The new salts exhibit significantly higher densities than those of the aforementioned heterocyclium(1+) salts of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> and CB<sub>11</sub>H<sub>12</sub><sup>-</sup> [12]. Reaction conditions, product yields, density values, certain salt melting/decomposition behaviors, and the general scope of the synthesis of binary heterocyclium salts of B<sub>12</sub>F<sub>12</sub><sup>2-</sup> are addressed in this paper.

## 2. Results and discussion

### 2.1. General comments

A long sought-after goal of synthetic chemistry has been the ability to rationally design chemical structures which will exhibit predictable chemical and physical properties for attaining desired chemical or physical behavioral responses [12,13,17]. Heterocyclic salts offer three different types of flexibility for achieving this goal. The cation ring structure or its pendant groups can be altered (e.g., 1-NH<sub>2</sub>-3-H-1,2,3-triazolium(1+) vs. 4-NH<sub>2</sub>-1-H-1,2,4-triazolium(1+))

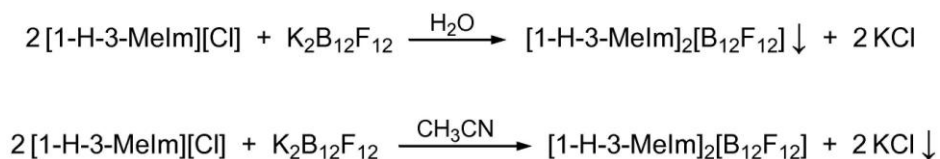
[12,13] or 1-NH<sub>2</sub>-3-H-1,2,3-triazolium(1+) vs. 1-NH<sub>2</sub>-3-Me-1,2,3-triazolium(1+)) when paired with a common anion [12]. The chemical structure of the anion can also be changed (e.g., a polyhedral borane(2-) anion vs. a carborane(1-) anion) when paired with an identical cation [12,13]. Furthermore, a cation with a different composition (with an identical anion), or an entirely different anion (with a common cation), can be substituted in a given salt (e.g., imidazolium(1+) vs. triazolium(1+) cation [12], or nitrate(1-) vs. a polyhedral borane(2-) anion [17]).

Tailoring the thermochemical initiation response of two bridged heterocyclium salts of borane(2-) anions, and of bridged heterocyclium(2+) nitrate(1-) salts, to rapid self-sustained combustions in air by altering the cation chemical structure, or by substitution of the anion, has been demonstrated experimentally [17] and was explained by an updated high-energy-material initiation-sensitivity concept [18]. Like the previously-reported bridged heterocyclium(2+) salts of B<sub>12</sub>F<sub>12</sub><sup>2-</sup> [8], the binary heterocyclium(1+) salts of B<sub>12</sub>F<sub>12</sub><sup>2-</sup> described in this paper provide additional examples in the flexibility of the heterocyclium(*n*+) system for rational structural design, predictable property modification, and the resultant tailoring of the chemical/physical behavior of this important class of salts.

### 2.1. Synthesis of new salts

The nine salts shown in Fig. 2 were synthesized using metathesis reactions similar to the example shown in Scheme 1 for the synthesis of salt **2**. Most of the metatheses were carried out on a small scale initially (e.g., 44–101 mg K<sub>2</sub>B<sub>2</sub>F<sub>12</sub>) using H<sub>2</sub>O as the solvent. As with the pre-

Scheme 1



viously reported binary [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] [12,13] or [heterocyclium][CB<sub>11</sub>H<sub>12</sub>] salts [12–16], the solubility of the particular B<sub>12</sub>F<sub>12</sub><sup>2-</sup> salt dictated whether H<sub>2</sub>O or CH<sub>3</sub>CN could be used as the solvent for a high-yield metathesis reaction [12,13]. It was found that salts **2**, **5**, and **6** could be prepared in good yield in either solvent. In contrast, salts **1** and **3** were best prepared using CH<sub>3</sub>CN (even small-scale reactions in this solvent gave good yields). Finally, salts **4** and **7–9** were best prepared using H<sub>2</sub>O as the solvent. The metathesis reaction solvent, reaction scale, yield, and melting/decomposition behavior of binary salts **1–4** and **6** are listed in Table 1.

The improved synthesis of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> reported in 2009 [19] made this reactant salt available in significantly larger quantities than if the original synthesis reported in 2003 had been used [7]. The larger-scale and shorter-reaction-time synthetic method was achieved by perfluorination of 10 g of K<sub>2</sub>B<sub>12</sub>H<sub>12</sub> to K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> in 74% yield and 99.5+% purity by continuously bubbling 20/80 F<sub>2</sub>/N<sub>2</sub> through a CH<sub>3</sub>CN solution of commercially-available K<sub>2</sub>B<sub>12</sub>H<sub>12</sub> using ordinary glassware [19]. The enhanced availability of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> permitted relatively large-scale metathesis reactions to be conducted in this work using 0.453–0.902 g quantities of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub>. This allowed salts **2**, **4**, and **6** to be prepared in quantities exceeding 1 gram in this work, as was also the case in the work reported in ref. [8].

Accomplishing these large-scale syntheses permitted reliable product yields and spectroscopic characterization data to be obtained for salts **2**, **4**, and **6**. Additionally, a direct comparison between two identical metathesis reactions was made using the same amount of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> and either H<sub>2</sub>O or CH<sub>3</sub>CN as the solvent to prepare salt **2** (see Table 1). The lower yield obtained from the metathesis reaction in H<sub>2</sub>O (i.e., 84% vs. 99% when CH<sub>3</sub>CN was the solvent) may be due to the fact that salt **2** is slightly soluble in H<sub>2</sub>O. After isolating the precipitated salt **2** (84% yield) by filtration (Scheme 1), evaporating the H<sub>2</sub>O filtrate resulted in a white solid residue that was partially soluble in DMSO-d<sub>6</sub>, leaving behind some insoluble KCl byproduct. Proton and <sup>13</sup>C NMR analyses of this clear, colorless DMSO-d<sub>6</sub> solution revealed the presence of the 1-Me-3-H-imidazolium(1+) cation, and an FTIR spectrum taken on this same white solid filtrate residue confirmed the presence of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> dianion by displaying two strong peaks at

1220 and 719  $\text{cm}^{-1}$  [19]. Both samples of salt **2**, whether synthesized in  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CN}$ , gave identical spectroscopic data consistent with the composition  $[\text{1-Me-3-H-imidazolium}]_2[\text{B}_{12}\text{F}_{12}]$ .

Salt **4** was prepared by reacting a stoichiometric amount of  $[\text{4-NH}_2\text{-1-H-1,2,4-triazolium}][\text{I}]$  with 0.902 g  $\text{K}_2\text{B}_{12}\text{F}_{12}$ . The digested solid was filtered and dried and afforded 1.03 grams of a fine white powder of **4** (90.0% yield). Spectroscopic analyses of this sample of **4** were consistent with the single-crystal X-ray determined structure of **4** determined using crystals prepared with a small-scale metathesis reaction. Salt **6** was prepared by reacting a stoichiometric amount of  $[\text{1-NH}_2\text{-3-H-1,2,3-triazolium}][\text{I}]$  with 0.901 g  $\text{K}_2\text{B}_{12}\text{F}_{12}$  under the same conditions just described to prepare salt **4**. This afforded, after filtering and drying, 1.06 grams of **6** as an off-white solid (92.3% yield). Proton and  $^{13}\text{C}$  NMR and FTIR spectroscopic data for this sample of **6** were consistent with the single-crystal X-ray structure of **6** determined from crystals prepared using a small-scale milligram (87.2 mg) metathesis reaction. The spectroscopic data between the large-scale and small-scale prepared samples of **6** also matched.

To minimize the presence of residual KX byproduct in these larger scale reactions ( $\text{X} = \text{Cl}, \text{Br}$ ) [8], the aqueous metatheses were conducted by dropwise addition of an aqueous solution of  $\text{K}_2\text{B}_{12}\text{F}_{12}$  to a refluxing aqueous solution of the heterocyclium(1+) halide. After refluxing for 5–8 minutes, during which precipitation of the desired  $[\text{heterocyclium}]_2[\text{B}_{12}\text{F}_{12}]$  perfluoroborane salt product **2**, **4**, or **6** occurred, the reaction suspension was cooled to room temperature prior to final isolation by filtration and subsequent vacuum drying. Samples of salt **2** prepared using either  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CN}$  as the metathesis solvent were analyzed for the presence of  $\text{Cl}^-$  by ion chromatography. In both cases the mass% of  $\text{Cl}^-$  was only 0.01%, demonstrating the level of purity that is possible using the metathesis reactions shown in Scheme 1.

The attempted synthesis of  $[\text{4-NH}_2\text{-1-H-1,2,4-triazolium}]_2[\text{B}_{12}\text{F}_{12}]$  instead produced  $[\text{4-NH}_2\text{-1-H-1,2,4-triazolium}]_2[\text{B}_{12}\text{F}_{12}]\cdot\text{4-NH}_2\text{-1,2,4-triazole}$  (**5**). The inclusion of the neutral 4- $\text{NH}_2$ -1,2,4-triazole molecule in salt **5** was first thought to result from an equilibrium between the reagent  $[\text{4-NH}_2\text{-1-H-1,2,4-triazolium}][\text{Cl}]$  and the free-base triazole in  $\text{H}_2\text{O}$ . However, when the same reaction was carried out in  $\text{CH}_3\text{CN}$ , the product was also salt **5**. Both of these perplexing

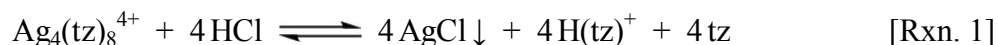
but reproducible results were confirmed by single crystal X-ray analysis. One might expect a higher density for salt **5** were it devoid of this neutral triazole molecule.

Small-scale aqueous metathesis reactions were used to prepare salts **7** and **8**, which crystallized with three or two H<sub>2</sub>O molecules per formula unit in their respective lattices (see Fig. 2). The presence of H<sub>2</sub>O molecules in the lattices of these salts precludes a detailed comparison of the packing of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions and the six-membered-ring pyrimidinium(1+) cations in **7**·3H<sub>2</sub>O or the bicyclic purinium(1+) cations in **8**·2H<sub>2</sub>O with the five-membered-ring heterocyclium(1+) cation salts **1–4** and **6**. In this regard the lattice H<sub>2</sub>O molecules in **7**·3H<sub>2</sub>O and **8**·2H<sub>2</sub>O are acting like the "extra" 1-NH<sub>2</sub>-1,2,3-triazole molecule in **5**, taking up what is presumably empty space in the lattice of B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions and protonated heterocyclium(1+) cations.

Although the expected binary salts **1–4** and **6** and the hydrated salts **7** and **8** could be readily formed using the metathesis reactions in Scheme 1, we were not able to isolate binary [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts using halide salts of the protonated heterocyclium(1+) cations **10<sup>+</sup>–13<sup>+</sup>**, shown in Fig. 3, as metathesis reagents. For cations **10<sup>+</sup>–12<sup>+</sup>**, it appears that the putative [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts are more soluble in H<sub>2</sub>O than K<sub>2</sub>B<sub>12</sub>F<sub>12</sub>. For cation **13<sup>+</sup>**, only the mixed-cation crystalline "half-salt" product [K][**13**][B<sub>12</sub>F<sub>12</sub>]·2H<sub>2</sub>O, which was characterized by a preliminary X-ray structure (not shown), was obtained using H<sub>2</sub>O as the solvent. (Note that a similar "half-salt" product with the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anion, [K][4-NH<sub>2</sub>-1-H-1,2,4-triazolium][B<sub>12</sub>H<sub>12</sub>], was recently reported [13].)

The previously reported CH<sub>3</sub>CN-trituration procedure [13], successfully used for water-soluble binary heterocyclium(1+) salts of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> and CB<sub>11</sub>H<sub>12</sub><sup>-</sup>, also was attempted, but without success. A different metathesis reaction was also tried in order to prepare the elusive binary salt [1-NH<sub>2</sub>-3-H-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (i.e., [**13**][B<sub>12</sub>F<sub>12</sub>]) by driving this metathesis reaction to completion through aqueous AgCl precipitation [13]. This metathesis reaction between [**13**][Cl] and [Ag<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>][B<sub>12</sub>F<sub>12</sub>] in H<sub>2</sub>O led not to the desired product but instead to the isolation of crystalline [Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub>][B<sub>12</sub>F<sub>12</sub>] (**9**) with a tetrameric tetracation,

which was characterized by single-crystal X-ray diffraction. Apparently the equilibrium shown in Rxn. 1 lies far to the left, precluding the precipitation of AgCl (tz = 1-NH<sub>2</sub>-1,2,3-triazole).



The new salts **2**, **4**, and **6**, prepared with the large-scale metathesis reactions, were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and FTIR spectroscopy. In one case, salt **6** prepared using a small-scale reaction had spectra that matched those recorded for a sample of **6** which was synthesized using a significantly larger-scale metathesis reaction. Samples of salt **2** prepared using either solvent were analyzed for the presence of Cl<sup>−</sup> by ion chromatography. In both cases the mass% of Cl<sup>−</sup> was only 0.01%, demonstrating the level of purity that is possible using the metathesis reactions shown in Scheme 1. Most of the new salts prepared using small-scale metathesis reactions were also compositionally characterized by single-crystal X-ray diffraction analysis (see below). The single-crystal X-ray structure of salt **7** was not of sufficient quality for publication, but analysis of a low-quality data set confirmed the trihydrate composition shown in Fig. 2.

## 2.2. X-ray structures of the new salts

Crystallographic data and structure refinement parameters for new B<sub>12</sub>F<sub>12</sub><sup>2−</sup> heterocyclium(1+) salts **1–6**, **8**, and **9** are listed in Table 2. Thermal ellipsoid plots of all eight formula units are shown in the Supplementary data. Portions of the structures of salts **1–6** that are relevant to the discussion below are shown in Figs. 4 and 5. These figures depict all atoms as spheres of arbitrary size for clarity. In addition, Figs. 4 and 5 depict the centroid of each B<sub>12</sub>F<sub>12</sub><sup>2−</sup> anion (i.e., the B<sub>12</sub> centroid, for which the symbol ⊙ is used) as a small sphere connected by dashed lines to other B<sub>12</sub> centroids in order to show the idealized rhombs formed by eight B<sub>12</sub>F<sub>12</sub><sup>2−</sup> anions in salts **1–6**. Selected solid-state structure parameters for B<sub>12</sub>F<sub>12</sub><sup>2−</sup> salts **1–6** and

for related  $\text{B}_{12}\text{H}_{12}^{2-}$  salts with the same cations, including the  $\odot\cdots\odot$  distances that define the anion rhombs, are listed in Table 3.

The recently published structures of  $[\text{K}_2(\text{H}_2\text{O})_2][\text{B}_{12}\text{F}_{12}]$  and  $[\text{K}_2(\text{H}_2\text{O})_4][\text{B}_{12}\text{F}_{12}]$  revealed a structural motif for  $\text{B}_{12}\text{F}_{12}^{2-}$  salts consisting of a rhomb of anions containing a pair of hydrated  $\text{K}^+$  cations. The  $\odot\cdots\odot$  distances in those rhombs ranged from 6.915 to 8.598 Å, which is comparable to the range of  $\odot\cdots\odot$  distances for salts **1–6**, 7.122–10.675 Å. In addition, the distance between the  $\text{K}^+$  cations within the rhombs in  $[\text{K}_2(\text{H}_2\text{O})_2][\text{B}_{12}\text{F}_{12}]$  and  $[\text{K}_2(\text{H}_2\text{O})_4][\text{B}_{12}\text{F}_{12}]$  are ca. 4.3 Å, which is the middle of the range of cation $\cdots$ cation distances in salts **1–6**, 3.589–5.708 Å (these distances, also listed in Table 3, are the shortest distances between the centroids of the five-membered rings of the heterocyclium(1+) cations in salts **1–6** and will hereinafter be referred to as cat $\cdots$ cat distances).

### 2.2.1. Imidazolium(1+) salts **1**, **2**, and **3**

A drawing of the rhombs of  $\text{B}_{12}\text{F}_{12}^{2-}$  centroids ( $\odot$ ) and their pairs of heterocyclium(1+) cations for each of these three salts is shown in Fig. 4. The rhomb for salt **1** contains parts of four 1-Et-3-Me-imidazolium(1+) cations that add up to two complete cations; the rhombs for salts **2** and **3** contain two complete 1-H-3-Me-imidazolium(1+) or H(imidazolium)(1+) cations, respectively, in the middle of their rhombs. The data in Table 3 demonstrate that as the imidazolium(1+) substituents change from Et/Me to H/Me to H/H the formula unit volumes and the  $\odot\cdots\odot$  and cat $\cdots$ cat distances all decrease and the density increases. The increase in density for the hypothetical transformation **1**  $\rightarrow$  **2**  $\rightarrow$  **3** is from 1.576 to 1.739 to 1.829 g cm $^{-3}$ , respectively.

Unlike the cation orientations in the structure of **1**, the five-membered rings of the two cations within the anion rhombs in **2** and **3** are nearly parallel: the dihedral angles of their least-squares planes with respect to one another are 3.6 and 2.5°, respectively. Furthermore, the perpendicular distances of the atoms of one five-membered cation ring to the least-squares plane of the other are 3.3–3.5 Å in both cases, producing a graphite-like separation of the two cations despite the repulsion of the positive charges on each ring.

### 2.2.1. Aminotriazolium(1+) salts **4**, **5**, and **6**

A drawing of the rhombs of  $\text{B}_{12}\text{F}_{12}^{2-}$  centroids ( $\odot$ ) and their heterocyclium(1+) cations for each of these three salts is shown in Fig. 5. The structures of salts **4** and **6**, like those of salts **2** and **3**, contain two complete heterocyclium(1+) cations within the rhombs, cat...cat distances of 4.647 Å in **4** and 5.287 Å in **6**. However, unlike the nearly parallel orientations of the cation five-membered rings in salts **2** and **3**, the dihedral angles between the least-squares cation rings in **4** and **6** are 56.7 and 52.7°, respectively.

The composition of salt **5**, and its solid-state structure, are different than those of salts **1–4** and **6**. In addition to the two 4-NH<sub>2</sub>-1-H-1,2,4-triazolium(1+) cations paired with each  $\text{B}_{12}\text{F}_{12}^{2-}$  anion, there is a molecule of neutral 4-NH<sub>2</sub>-1,2,4-triazole in the formula unit. There is a five-membered ring approximately centered on each of the six faces of the anion rhomb, four 4-NH<sub>2</sub>-1-H-1,2,4-triazolium(1+) cations and two 4-NH<sub>2</sub>-1,2,4-triazoles (only two cations and one neutral triazole are shown in Fig. 5 for clarity). Not surprisingly, the shortest cat...cat distance in salt **5**, which is 5.445 Å, is longer than the shortest distance between a cation centroid and the five-membered ring centroid of the neutral triazole molecule, which is 4.936 Å. Also not surprisingly, the interactions between the triazolium(1+) cations and the neutral triazole molecule in salt **5** are N–H...N hydrogen bonds ((N)H...N = 1.911 Å, N–H...N = 166.5°, N...N = 2.747 Å; (N)H...N = 2.025 Å, N–H...N = 168.5°, N...N = 3.001 Å; neither of these hydrogen bonds involve NH<sub>2</sub> groups).

The density of each of the [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts **1**, **2**, **4**, and **6** can be compared to the density of the corresponding [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] salt (see Table 3). As with perfluorocarbon versus analogous hydrocarbon organic compounds, the heterocyclium(1+) B<sub>12</sub>F<sub>12</sub><sup>2–</sup> salts are more dense than the corresponding heterocyclium(1+) B<sub>12</sub>H<sub>12</sub><sup>2–</sup> and CB<sub>11</sub>H<sub>12</sub><sup>–</sup> salts (for example, the densities of benzene and hexafluorobenzene are 0.877 and 1.61 g cm<sup>–3</sup>, respectively, and the densities of *n*-hexane and perfluoro-*n*-hexane are 0.655 and 1.67 g cm<sup>–3</sup>, respectively). A comparison of the structures of [1-H-3-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**2**) and

[1-H-3-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] [12] is especially appropriate. Interestingly, the anion rhombs are very similar in the two salts: the  $\odot \cdots \odot$  distances are ca. 7.5, 8.0, and 9.4 Å in both salts, and the acute  $\odot \cdots \odot \cdots \odot$  angles are 65.0, 77.8, and 84.9° in **2** and 63.9, 66.1, and 89.7° in the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> salt, demonstrating that the relative sizes of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> and B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anions are quite similar (typical B–F and B–H distances in these anions are ca. 1.38 and 1.12 Å and typical  $\odot \cdots F$  and  $\odot \cdots H$  distances are ca. 3.08 and 2.80 Å, respectively). In addition, the cat $\cdots$ cat distances are also similar (they only differ by 11%), 4.585 Å in **2** and 4.113 Å in the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> salt. Nevertheless, the densities differ by a factor of 1.571 (1.739 vs. 1.107 g cm<sup>-3</sup>), mostly because the molar mass of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> and B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anions differ by a factor of 2.52 (357.72 vs. 141.84 g mol<sup>-1</sup>).

Comparison of imidazolium(1+) salts **1–3** and 1,2,4-triazolium(1+) salts **4** and **5** reveals that the salt density is higher when the cation is a protonated heterocyclium(1+) cation instead of an alkylated heterocyclium(1+) cation. In fact, there is a nearly linear relationship between the salt density and the shortest cat $\cdots$ cat distance for these five B<sub>12</sub>F<sub>12</sub><sup>2-</sup> salts, as shown in Fig. 6. Interestingly, there is no such correlation for the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> salts: the data in Table 3 show that the densities, and the shortest cat $\cdots$ cat distances, are nearly the same for [1-Et-3-Me-imidazolium][B<sub>12</sub>H<sub>12</sub>] (1.101 g cm<sup>-3</sup> and 4.119 Å) and [1-H-3-Me-imidazolium][B<sub>12</sub>H<sub>12</sub>] (1.107 g cm<sup>-3</sup> and 4.113 Å), despite the fact that the 1.576 g cm<sup>-3</sup> density of [1-Et-3-Me-imidazolium][B<sub>12</sub>F<sub>12</sub>] (**1**) is more than 10% lower than the 1.739 g cm<sup>-3</sup> density of [1-H-3-Me-imidazolium][B<sub>12</sub>F<sub>12</sub>] (**2**).

### 2.2.3. Salt 8

The packing of 2,6-(NH<sub>2</sub>)<sub>2</sub>-1-H-purinium(1+) cations and H<sub>2</sub>O molecules inside the rhomb of eight B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions in the structure of [2,6-(NH<sub>2</sub>)<sub>2</sub>-1-H-purinium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]·2H<sub>2</sub>O (**8**) is shown in Fig. 7. The planes of the two purinium(1+) cations are nearly parallel (dihedral angle of only 0.2°) and the C and N atoms of the fused-ring system of one cation are ca. 3.4 Å from the least-squares plane of the C and N atoms that make up the fused-ring system of the other cation,

once again a graphite-like interaction of the two cations. The H<sub>2</sub>O molecules form (N)H $\cdots$ O hydrogen bonds with an H $\cdots$ O distances of 1.78 Å and N–H $\cdots$ O angles of 154° and two (O)H $\cdots$ F hydrogen bonds with H $\cdots$ F distances of 2.12 and 2.21 Å. The  $\odot\cdots\odot$  distances in the structure of **8** are 7.423 ( $\times 2$ ) and 12.241 Å.

Fig. 7 also shows a drawing of the structure of salt **3** for comparison. These drawings emphasize the dovetail-like packing of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions. The  $\odot\cdots\odot$  distances for the two anions shown are 7.423 Å for **8** and 7.122 Å for **3**. The angles between the two highlighted F–B–B–F planes in each drawing are 78.7° for **8** and 90° for **3**. The F $\cdots$ F distances shown are 2.779, 3.193, 3.689, and 3.796 Å in **8** and 2.908 ( $\times 2$ ) and 3.108 Å ( $\times 2$ ) in **3** (note that twice the van der Waals radius of an F atom is ca. 3.0 Å). This dovetail-like packing was also observed in the structures of [K(H<sub>2</sub>O)<sub>n</sub>]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (*n* = 1, 2) [10] and in heterocyclium(1+) salts of the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> and CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anions [12,13].

#### 2.2.4. Salt **9**

The packing of the discrete Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub><sup>4+</sup> cations and B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions in the structure of [Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub>][B<sub>12</sub>F<sub>12</sub>]<sub>2</sub> (**9**) is complicated and will not be discussed here. Instead, we describe the structure of the tetrameric tetracation, shown in Fig. 8, and compare it to two similar Ag<sub>4</sub>(triazole)<sub>n</sub><sup>4+</sup> tetracations [20,21]. Relevant structural parameters are listed in Table 4. The four Ag<sup>+</sup> ions in each tetracation in **9** are rigorously coplanar, with Ag $\cdots$ Ag distances of 3.764(2) and 3.858(2) Å and Ag $\cdots$ Ag $\cdots$ Ag angles of 65.8(1) and 114.2(1)°. These are similar to the corresponding parameters in the structures of [Ag<sub>4</sub>(4-NH<sub>2</sub>-1,2,4-triazole)<sub>7</sub>][ClO<sub>4</sub>] [20] and [Ag<sub>4</sub>(4-(3-C<sub>6</sub>H<sub>4</sub>OH)-1,2,4-triazole)<sub>6</sub>][NO<sub>3</sub>]<sub>4</sub>·4H<sub>2</sub>O [21].

An interesting feature of the structure of the tetrameric Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub><sup>4+</sup> cation in **9** is that the Ag1 cations are only bonded to the more basic N3 atoms of three  $\mu$ -(1-NH<sub>2</sub>-1,2,3-triazole)- $\kappa$ N2: $\kappa$ N3 ligands, with Ag1–N3 distances of 2.211(3), 2.238(3), and 2.322(4) Å. The Ag2 cations, on the other hand, are bonded to the less basic N2 atoms of the three bridging triazole ligands, with Ag2–N2 distances of 2.263(3), 2.404(3), and 2.492(4) Å. Probably because

of the weaker bonding between Ag<sub>2</sub> and the three bridging triazole ligands, each Ag<sub>2</sub> cation is also coordinated to a terminal 1-NH<sub>2</sub>-1,2,3-triazole ligand through N3, with a Ag<sub>2</sub>–N3 distance of 2.255(3) Å. If not for this terminal triazole ligand, the sum of bond-valences [22] for Ag<sub>2</sub> would be significantly less than 1.0 (an Ag–N distance of 2.255 Å corresponds to a bond valence of 0.335 [22]).

### 3. Conclusions

Five new binary [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts **1-4** and **6** were synthesized in 84–99% isolated yield. In addition, three salts **5**, **7** and **8** that also contained neutral molecules, either a triazole or H<sub>2</sub>O, were also prepared. These are the first salts that contain heterocyclium(1+) cations paired with the icosahedral B<sub>12</sub>F<sub>12</sub><sup>2-</sup> perfluorododecaborate dianion. Open-air benchtop double-displacement (metathesis) reactions using common laboratory glassware were employed, in which a stoichiometric amount of heterocyclium(1+) halide salt was treated with K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> in either H<sub>2</sub>O or CH<sub>3</sub>CN solvent. Depending on the particular salt, the synthesis was carried out at a temperature that ranged from room temperature to 100 °C and on a scale that ranged from 44 mg of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> to nearly 1 g of this salt.

Compared with previously reported analogous heterocyclium cation(1+) salts of the icosahedral B<sub>12</sub>H<sub>12</sub><sup>2-</sup> borane and CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anions that were synthesized in a similar manner, the scope of the reaction for binary [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] perfluoroborane salts was found to be more limited. Four different protonated heterocyclium(1+) cations each form the previously reported [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] and the [heterocyclium][CB<sub>11</sub>H<sub>12</sub>] salts, but only one analogous [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salt **5** was isolated. But unlike the protonated [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] and [heterocyclium]<sub>2</sub>[CB<sub>11</sub>H<sub>12</sub>] analogs of **5**, [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] product salt **5** also incorporated a neutral heterocycle molecule in its structure. The reduction in reaction scope resulted from the lower solubility of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> relative to several putative [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] product salts that could not be isolated. In these cases, the unreacted K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> reactant salt was usually the solid recovered.

Larger protonated heterocyclic cations, a six-membered pyrimidinium and a fused bicyclic purinium species, gave new sparingly-soluble [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts **7** and **8**, respectively, that could be isolated from the aqueous metathesis reaction mixture, although both contained solvent molecules (H<sub>2</sub>O) in the crystalline salts. In one case an isolated mixed cation [heterocyclium][K][B<sub>12</sub>F<sub>12</sub>] perfluoroborane "half salt" product was isolated instead of the expected [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salt product. This apparently resulted from this "half salt" product being less soluble in the H<sub>2</sub>O reaction solvent than were either the K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> reactant salt or the desired [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] product. One "half salt" [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] product recently has appeared in the literature. Three binary [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] perfluoroborane salt products (**2**, **4**, **6**) were isolated from three different methylated heterocyclium(1+) cations using either H<sub>2</sub>O or CH<sub>3</sub>CN solvent, and either solvent could be used for salt **2**. One binary dialkylated [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] product salt **1** was obtained. All four alkylated product salts **1**, **2**, **4**, and **6** have corresponding binary [heterocyclium][B<sub>12</sub>H<sub>12</sub>] and [heterocyclium][CB<sub>11</sub>H<sub>12</sub>] product analogs that have been reported.

There were two anomalous observations made during the syntheses described in this work. First, when attempting to synthesize [4-NH<sub>2</sub>-1-H-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] in either H<sub>2</sub>O or CH<sub>3</sub>CN as the solvent, the neutral triazole molecule [4-NH<sub>2</sub>-1,2,4-triazole] was incorporated into the product salt structure (i.e., the composition was [4-NH<sub>2</sub>-1-H-1,2,4-triazolium]<sub>2</sub>[4-NH<sub>2</sub>-1,2,4-triazole][B<sub>12</sub>F<sub>12</sub>] (**5**)). Second, an attempt was made to drive an aqueous metathesis reaction to completion with AgCl precipitation. Reacting the [4-NH<sub>2</sub>-1-H-1,2,4-triazolium][Cl] salt with [Ag(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] as the source of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anion in place of K<sub>2</sub>B<sub>12</sub>F<sub>12</sub>, resulted in the Ag<sup>+</sup> ions coordinating to the N atoms of neutral triazole molecules to give a complex tetracation that formed a unique high density salt [Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub>][B<sub>12</sub>F<sub>12</sub>]<sub>2</sub> (**9**).

The density of individual [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] perfluorododecaborane salts were significantly higher than are the recently-published analogous [heterocyclium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] and [heterocyclium][CB<sub>11</sub>H<sub>12</sub>] salts. Additionally, protonated [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts displayed a higher density than did analogous alkylated [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts. In fact, an

interesting linear correlation between salt density and cat···cat separation was discovered for a set of five  $B_{12}F_{12}^{2-}$  salts **1-4**, and **6** that does not appear to be followed for  $B_{12}H_{12}^{2-}$  salts.

## 4. Experimental

### 4.1. General Comments.

**Caution!** While no special protective equipment or handling procedures were used with salts (**1-9**), these are high energy materials, and the analogous binary heterocyclium salts of  $B_{12}H_{12}^{2-}$  and  $CB_{11}H_{12}^{-}$  can be initiated to rapid energy-releasing phenomena. Thermal initiation can occur on a hot plate surface ( $>275\text{ }^{\circ}\text{C}$ ) to rapid combustion with protonated binary heterocyclium(1+) salts [17] and bridged heterocyclium(2+) salts of  $B_{12}H_{12}^{2-}$  [17]. Recent standard impact, friction, and electrostatic discharge (ESD) hazards testing conducted on the binary salt  $[1\text{-NH}_2\text{-3-Me-1,2,3-triazolium}]_2[B_{12}H_{12}]$ , the analogue of the new salt  $[1\text{-NH}_2\text{-3-Me-1,2,3-triazolium}]_2[B_{12}F_{12}]$ , gave a 100% impact non-initiation ("no-go") response at 156 kg cm, a 21.6 kg cm friction minimum non-initiation response, but initiated electrostatically at 0.040 J on an ESD test [13]. These two 100% "No-Go" impact initiation values compare with known explosives for which the following more sensitive 50% initiation kg cm values are available: CL-20 at 33; PETN at 67; HMX at 115; and RDX at 117 kg cm. One bridged heterocyclium(2+) salt of  $B_{12}F_{12}^{2-}$ , the only salt of  $B_{12}F_{12}^{2-}$  tested to date, gave a minimum non-initiation impact at 147 kg cm (100% "no-go" non-initiation value), a minimum non-initiation friction response at 21.6 kg cm, but initiated at 0.090 J in the ESD test [13].

All water used was deionized water obtained from a Millipore MILL-Q Reagent Grade Water System at the 18 M $\Omega$  cm level of purity. All organic solvents were commercially available as either Reagent Grade or HPLC purity and were used as received.

With one exception, the neutral heterocyclic compounds used to synthesize  $B_{12}F_{12}^{2-}$  salts **1-9** were commercially available and were used as received. The exception is the compound 1-NH<sub>2</sub>-1,2,3-triazole, which was prepared using a published procedure [23]. Conversion of each neutral heterocycle to the corresponding hydrochloride or *N*-methylated iodide salt was carried

out as previously described (see Supplemental Information) [12] and detailed below. The heterocyclium(1+) hydrochloride salts were obtained from the commercial free bases via treatment with concentrated aqueous HCl in ethanol at 25 °C, followed by removal of all volatiles by rotary evaporation and drying under vacuum ( $\leq 0.1$  mTorr). The remaining solids were recrystallized from a minimum amount of hot 2-propanol. In some cases the addition of diethyl ether after the onset of crystallization resulted in a slightly higher yield. The microcrystalline products were filtered, washed with diethyl ether, and dried under vacuum.

An alternative method is possible for the synthesis of the hydrochloride of 4-NH<sub>2</sub>-1,2,4-triazole. This salt can also be synthesized in a 250 mL round-bottom flask by adding 2.50 g (29.7 mmol) of 4-NH<sub>2</sub>-1,2,4-triazole and 2.50 mL (29.9 mmol) of 37% aqueous HCl to 50 mL MeOH and letting the mixture stand at room temperature for two days. High vacuum Removal of the solvent under vacuum afforded 3.53 g of a thick syrup that was recrystallized from hot MeOH and Et<sub>2</sub>O. Filtration, rinsing with a small portion of Et<sub>2</sub>O, and vacuum drying afforded 2.24 g of microcrystalline [4-NH<sub>2</sub>-1-H-1,2,4-triazolium][Cl] (62.6% yield). The methylated heterocyclium(1+) iodide salts were obtained by reaction of the neutral free-base heterocycle with excess CH<sub>3</sub>I in EtOH at room temperature for at least 12 h followed by removal of all volatiles by rotary evaporation (the reaction vessel was wrapped with foil to protect the reaction mixture from direct light). If necessary, some of these salts were recrystallized from MeOH. The preparation of [H(imidazolium)][Cl] for the synthesis of salt **3** was achieved by bubbling dry HCl gas (10–15 mL/min flow rate) through an anhydrous CHCl<sub>3</sub> solution of imidazole for 30 min. The white needle-shaped crystals that formed were filtered, washed with anhydrous CHCl<sub>3</sub>, and dried under vacuum. The preparation of [1-Et-3-Me-imidazolium][Br] for the synthesis of salt **1** was achieved by reacting EtBr (23.1 mmol) and 1-Me-imidazole (11.2 mmol) in refluxing anhydrous benzene (20 mL) for 2 h. Filtering the cooled reaction mixture, washing the white crystalline product, and drying under vacuum afforded [1-Et-3-Me-imidazolium][Br] in 64% yield. The salt [Ag(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] was prepared as previously described [24].

#### 4.2. Spectroscopy, X-ray crystallography, ion chromatography, and melting points

A Bruker Avance 400 Digital NMR instrument was used to obtain both  $^1\text{H}$  and  $^{13}\text{C}$  spectra. FTIR spectra were taken as powder samples in air using a Nicolet 6700 Spectrometer equipped with an HATR optical system. Only the significant peaks that were observed are listed below. The FTIR spectrum of  $\text{K}_2\text{B}_{12}\text{F}_{12}$  salt exhibits only two strong peaks at  $1221\text{ cm}^{-1}$  ( $\nu(\text{BF})$ ) and  $719\text{ cm}^{-1}$  ( $\nu(\text{BB})$ ) [19]. The presence of  $\text{B}_{12}\text{F}_{12}^{2-}$  was confirmed in  $[\text{heterocyclium}]_2[\text{B}_{12}\text{F}_{12}]$  salts **2**, **4**, and **6** by the presence of two strong peaks at ca.  $1220$  and ca.  $720\text{ cm}^{-1}$  in their respective FTIR spectra.

Single-crystal X-ray diffraction data for salts **2**, **4–6**, **8**, and **9** were collected at Edwards AFB using a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the  $\chi$ -axis fixed at  $54.74^\circ$  using  $\text{Mo K}\alpha$  or  $\text{Cu K}\alpha$  radiation from a fine-focus tube. The goniometer head, equipped with a Nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. Diffraction data for salts **1** and **3** were collected at Colorado State University using a Bruker Kappa APEX II CCD diffractometer at  $110(2)\text{ K}$  employing  $\text{Mo K}\alpha$  radiation (graphite monochromator). Unit cell parameters were obtained from least-squares fits to the angular coordinates of all reflections, and intensities were integrated from a series of frames ( $\omega$  and  $\varphi$  rotation) covering more than a hemisphere of reciprocal space. Absorption and other corrections were applied using SADABS [25]. The structures were solved using direct methods and refined (on  $F^2$  using all data) by a full-matrix, weighted least-squares process. Standard Bruker control and integration software (APEX II) was employed [26], and Bruker SHELXTL software was used for structure solution, refinement, and molecular graphics [27]. Crystal data and refinement details for salts **1–6**, **8**, and **9** are listed in Table 2.

For ion chromatography  $\text{Cl}^-$  analyses, each sample was weighed to  $0.01\text{ mg}$  and diluted to  $25\text{ mL}$  in a class B centrifuge tube with  $18\text{ M}\Omega\text{ cm}$  deionized water. The samples that were not readily soluble were heated to  $80\text{ }^\circ\text{C}$  with a reflux cap. All solution transfers and injections were accomplished with sterile syringes and syringe filters (IC Millex LG filter unit  $0.2\text{ }\mu\text{m}$ ). A four-point linear calibration curve was generated using a blank deionized water solution, followed by

a 0.1, 1, and 5 ppm ( $\mu\text{g g}^{-1}$ ) NIST traceable  $\text{Cl}^-$  standard where the peak area was determined for each chloride standard solution. Lower detection limits (LDL) and lower quantitation limits (LQL) were determined using seven individually prepared blanks consisting only of deionized  $\text{H}_2\text{O}$  (LDL = 3 times and LQL = 5 times the standard deviation of the seven blank runs). Concentrations were calculated by comparing peak area response versus the linear calibration graph and are corrected for dilution.

Melting points were determined using a Stanford Research Systems OptiMelt MPA100-Automated Melting Point Apparatus equipped with digital image video playback software.

#### 4.3. Small-scale $\text{CH}_3\text{CN}$ solvent synthesis procedure

The heterocyclium halide salt was dissolved in  $\text{CH}_3\text{CN}$  and mixed with a  $\text{CH}_3\text{CN}$  solution of  $\text{K}_2\text{B}_{12}\text{F}_{12}$  at room temperature to form a white KX precipitate ( $\text{X} = \text{Cl}, \text{Br}$ ). The solution was filtered and dried to give the desired binary  $[\text{heterocyclium}]_2[\text{B}_{12}\text{F}_{12}]$  salt, which was subsequently recrystallized from  $\text{CH}_3\text{CN}$ .

##### 4.3.1. $[1\text{-Et-3-Me-imidazolium}]_2[\text{B}_{12}\text{F}_{12}]$ (**1**)

Solutions of  $[1\text{-Et-3-Me-imidazolium}][\text{Br}]$  (0.088 g, 0.45 mmol) in 2 mL  $\text{CH}_3\text{CN}$  and  $\text{K}_2\text{B}_{12}\text{F}_{12}$  (0.10 mg, 0.22 mmol) in 2 mL  $\text{CH}_3\text{CN}$  were mixed at room temperature, affording 0.13 g of salt **1** (90% yield). Single-crystal X-ray diffraction analysis confirmed the composition of this salt.

##### 4.3.2. $[\text{H}(\text{imidazolium})]_2[\text{B}_{12}\text{F}_{12}]$ (**3**)

Solutions of  $[\text{H}(\text{imidazolium})][\text{Cl}]$  (0.048 g, 45 mmol) in 2 mL  $\text{CH}_3\text{CN}$  and  $\text{K}_2\text{B}_{12}\text{F}_{12}$  (0.10 mg, 0.22 mmol) in 2 mL  $\text{CH}_3\text{CN}$  were mixed at room temperature, affording 0.10 g of salt **3** (93% yield). Single-crystal X-ray diffraction analysis confirmed the composition of this salt.

##### 4.3.3. $[4\text{-NH}_2\text{-1-H-1,2,4-triazolium}]_2[\text{triazole}][\text{B}_{12}\text{F}_{12}]$ (**5**)

The compounds [4-NH<sub>2</sub>-1-H-1,2,4-triazolium][Cl] (20.1 mg, 0.167 mmol) and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (36.4 mg, 0.0835 mmol) together which were triturated with 5 × 8 mL of boiling CH<sub>3</sub>CN. The solution was cooled and the solvent removed under vacuum to yield 48.9 mg (95.7% yield) of off-white solid (95.7%). The solid was dissolved in a mixture of 1 mL CH<sub>3</sub>CN and 40 mL Et<sub>2</sub>O, and after standing overnight in a dessicator this solution deposited crystals of **5** suitable for single crystal X-ray diffraction analysis which revealed that one neutral 4-NH<sub>2</sub>-1-H-1,2,4-triazole molecule occupied the formula unit.

#### 4.3.4. [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**6**)

The compounds [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium][I] (0.0904 g, 0.400 mmol) and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (87.2 mg, 0.200 mmol) were each dissolved in a minimum amount of CH<sub>3</sub>CN at room temperature. The two solutions were mixed and the solvent was removed under vacuum to yield 0.179 g of a solid containing some KI byproduct. The crude solid dissolved in 1.24 mL H<sub>2</sub>O, refluxed, and cooled, producing crystals of **6** used for single crystal X-ray diffraction analysis. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub> (δ 2.50)): δ 8.74 (d<sub>ovlap.</sub>, 2H); 8.06 (d<sub>ovlap.</sub>, 2H); 8.82 (s, 4H); 4.21 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub> (δ 39.51)): δ 132.54, 126.84, 39.63 (shoulder on DMSO-d<sub>6</sub> peak δ 39.72); CD<sub>3</sub>CN (δ 1.39), δ 132.22, 129.58, 41.12. HATR-FTIR: 3375, 3309, 3185, 3166, 1624, 1535, 1434, 1396, 1330, 1222 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 1091, 1029, 948, 797, 725 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 667, 630 cm<sup>-1</sup>. These spectroscopic data are identical to those listed for salt **6** in Section 4.6.3, below.

#### 4.4. Small-scale H<sub>2</sub>O solvent synthesis procedure

The [heterocyclium][halide] salt and K<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] were mixed as solids into one flask. The mixture was dissolved in a minimum amount of H<sub>2</sub>O and warmed if necessary, usually below the boiling point. The solution was cooled to room temperature and placed into a refrigerator (3.5 °C) overnight or until crystals formed. This generally produced crystals suitable for single-

crystal X-ray diffraction analysis. Otherwise suitable crystals were obtained with solvent removal followed by recrystallization.

#### 4.4.1. *[4-NH<sub>2</sub>-1-Me-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (4)*

The compounds *[4-NH<sub>2</sub>-1-Me-1,2,4-triazolium][I]* (42.5 mg, 0.329 mmol) and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (43.6 mg, 0.100 mmol) were dissolved in 0.54 mL H<sub>2</sub>O and heated. Cooling gave crystals of **4** suitable for single-crystal X-ray diffraction analysis.

#### 4.4.2. *[4-NH<sub>2</sub>-1H-1,2,4-triazolium]<sub>2</sub>[4-NH<sub>2</sub>-1,2,4-triazole][B<sub>12</sub>F<sub>12</sub>] (5)*

The compounds *[4-NH<sub>2</sub>-1-H-1,2,4-triazolium][Cl]* (17.2 mg, 0.143 mmol) and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (43.6 mg, 0.100 mmol) were dissolved in 5 mL H<sub>2</sub>O and heated to 95 °C for 15 min. The solvent was removed under vacuum (ca. 18 mTorr) for 12 h and the resultant solid was redissolved in 1 mL H<sub>2</sub>O and placed in a refrigerator (3.5 °C) overnight. This afforded crystals of **5** suitable for single-crystal X-ray diffraction analysis which revealed that one neutral 4-NH<sub>2</sub>-1-H-1,2,4-triazole molecule occupied the formula unit.

#### 4.4.3. *[2,4,6-(NH<sub>2</sub>)<sub>3</sub>-1-H-pyrimidinium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (7)*

The compounds *[2,4,6-(NH<sub>2</sub>)<sub>3</sub>-1-H-pyrimidinium][Cl]* (64.6 mg, 0.400 mmol) and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (87.2 mg, 0.200 mmol) were dissolved in 3 mL H<sub>2</sub>O, brought to a boil, and cooled. The cooled solution deposited crystals of **7**·3H<sub>2</sub>O that were used for a preliminary X-ray diffraction study.

#### 4.4.4. *[2,6-diamino-1-H-purinium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (8)*

The compounds *[2,6-(NH<sub>2</sub>)<sub>2</sub>-1-H-purinium][Cl]* (74.6 mg, 0.400 mmol) and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (87.2 mg, 0.200 mmol) were dissolved in 3 mL H<sub>2</sub>O and brought to a boil. When cooled, this solution deposited crystals of **8**·2H<sub>2</sub>O suitable for single crystal X-ray diffraction analysis.

#### 4.4.5. *[Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub>][B<sub>12</sub>F<sub>12</sub>]<sub>2</sub> (9)*

The compounds [1-NH<sub>2</sub>-3-H-1,2,3-triazolium][Cl] (24.1 mg, 0.280 mmol) and [Ag(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (73.7 mg, 0.0999 mmol) were dissolved in 7 mL water and filtered through Celite. Solvent removal under high vacuum gave 42.4 mg (38.8% yield) of a solid which was dissolved in EtOH, filtered, and recrystallized from EtOH to give crystals of **9** suitable for single-crystal X-ray diffraction analysis.

#### 4.5. Large-scale CH<sub>3</sub>CN solvent synthesis of [1-Me-3-H-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**2**)

In a reaction flask containing a Teflon-coated magnetic stirring bar, [H(MeIm)][Cl] (0.254 g, 2.15 mmol) was dissolved in 5 mL CH<sub>3</sub>CN at room temperature. K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (0.454 g, 1.04 mmol) was dissolved in 4 mL CH<sub>3</sub>CN at room temperature in a second glass vessel. The K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> solution was added during 4 min to the stirred reaction flask solution using a disposable pipette, forming a precipitate. The second glass vessel was rinsed with 2 × 0.5 mL portions CH<sub>3</sub>CN, each of which was added to the stirred reaction flask during 1 min for a total addition time of 6 min. The suspension was stirred at room temperature for 17 h, then filtered using Celite to remove the white solid KCl byproduct. The CH<sub>3</sub>CN solvent filtrate was removed by rotary evaporation and gave an off-white solid. Removal of the volatiles under high vacuum at 65 °C (24 h) in an Electrothermal ChemDry<sup>®</sup> apparatus gave 0.540 g (98.9% yield) of a light tan solid. <sup>1</sup>H NMR (400 MHz; DMSO-d<sub>6</sub> (δ 2.50)): δ 14.17 (bd s, 2H); 9.03 (s, 2H); 7.69–7.68 (m, 2H); 7.66 (m, 2H); 3.86 (s, 6H). <sup>13</sup>C NMR (100 MHz; DMSO-d<sub>6</sub> (δ 39.51)): δ 135.82, 123.16, 119.78, 35.42. HATR-FTIR: 3397, 3355, 3178, 3122, 3078, 1640, 1585, 1443, 1329, 1306, 1218 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 1142, 1104, 1082, 1008, 874, 844, 763, 723 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 697, 616 cm<sup>-1</sup>. An aqueous synthesis of this salt **2** conducted on the same scale is described in paragraph 4.6.1.

#### 4.6. Large-scale H<sub>2</sub>O solvent synthesis procedure

The [heterocyclium][halide] salt was dissolved in a minimum volume of H<sub>2</sub>O in a 25 mL 14/20 single-necked recovery flask reaction vessel containing a Teflon-coated stirring bar. The flask was connected to a water-cooled reflux condenser and the solution was stirred and heated

to reflux in a 107–108 °C oil bath for 5 min. At this time, an aqueous solution of  $\text{K}_2\text{B}_{12}\text{F}_{12}$  that had been prepared in a minimum amount of warm  $\text{H}_2\text{O}$  in a 15 mL single-necked pear-shaped flask was added dropwise to the reaction flask, during 5–7 min, through the center of the reflux condenser using a disposable pipette, at which point a precipitate was observed. The pear-shaped flask that previously contained the  $\text{K}_2\text{B}_{12}\text{F}_{12}$  solution was rinsed with  $2 \times 1$  mL portions of  $\text{H}_2\text{O}$ , each of which were added dropwise to the refluxing reaction mixture. After an additional 5 min, the cloudy reaction mixture was cooled to room temperature and placed in a 3.5 °C refrigerator overnight. Vacuum filtration, rinsing the solid cake with  $2 \times 1$  mL of 3.5 °C  $\text{H}_2\text{O}$  and air-drying in the Büchner funnel at room temperature for ca. 1 h gave a semi-dry solid. The solid was placed into a 4 dram bottle and dried at 65 °C under vacuum (ca.  $10^{-4}$  Torr) in a Electrothermal ChemDry<sup>®</sup> apparatus for 18–55 h to yield the desired anhydrous salt.

#### 4.6.1. [1-Me-3-H-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (2)

[H(MeIm)][Cl] (0.254 g, 2.14 mmol) in 1 mL  $\text{H}_2\text{O}$  and the  $\text{K}_2\text{B}_{12}\text{F}_{12}$  (0.453 g, 1.04 mmol) in 4 mL  $\text{H}_2\text{O}$  was added dropwise over 7 min., then cooled 24 h in the refrigerator, filtered, and vacuum dried 24 h. Yield: 0.460 g (84.4%) of a slightly off-white solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub> (δ 2.50)): δ 14.15 (bd. s, 2H); 9.03 (s, 2H), 7.68 (m, 2H); 7.66 (m, 2H); 3.86 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub> (δ 39.51)): δ 135.81, 123.15, 119.77, 35.42. HATR-FTIR: 3398, 3355, 3179, 3124, 3087, 1640, 1585, 1552, 1442, 1328, 1307, 1216 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 1141, 1104, 1080, 1008, 877, 843, 763, 719 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 695, 615 cm<sup>-1</sup>.

#### 4.6.2. [4-NH<sub>2</sub>-1-Me-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (4)

[4-NH<sub>2</sub>-1-Me-1,2,4-triazolium][I] (0.964 g, 4.27 mmol) in 2 mL  $\text{H}_2\text{O}$  and  $\text{K}_2\text{B}_{12}\text{F}_{12}$  (0.902 g, 2.07 mmol) in 8 mL  $\text{H}_2\text{O}$  was added dropwise over 5 min., then cooled 21.5 h in the refrigerator, filtered, and vacuum dried 18.5 h. Yield: 1.03 g (90.0%) of a slightly off-white solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub> (δ 2.50)): δ 10.06 (s, 2H); 9.16 (s, 2H); 6.95 (s, 4H); 4.02 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub> (δ 39.51)): δ 145.04, 142.95, unknown (3<sup>rd</sup> peak masked

by DMSO and CD<sub>3</sub>CN internal standard), 146.13, 143.95, 118.41 (CD<sub>3</sub>CN), 40.24. HATR-FTIR: 3386, 3317, 3159, 3120, 1620, 1582, 1567, 1434, 1407, 1220 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 1170, 1072, 993, 980, 942, 891, 722 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 659, 621 cm<sup>-1</sup>.

#### 4.6.3. [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**6**)

[1-NH<sub>2</sub>-3-Me-1,2,3-triazolium][I] (0.964 g, 4.26 mmol) in 2 mL H<sub>2</sub>O and K<sub>2</sub>B<sub>12</sub>F<sub>12</sub> (0.901 g, 2.07 mmol) in 7 mL H<sub>2</sub>O was added dropwise over 5 min., then cooled 18.5 h in the refrigerator, filtered, and vacuum dried for 54.5 h. Yield: 1.06 g (92.3%) of a light tan solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub> (δ 2.50): δ 8.74 (d<sub>ovlap.</sub>, 2H); 8.60 (d<sub>ovlap.</sub>, 2H); 8.28 (s, 4H); 4.21 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub> (δ 39.51)): δ 131.52, 126.83, unknown (3<sup>rd</sup> peak masked by DMSO and CD<sub>3</sub>CN internal standard), 132.23, 129.59, 41.13. HATR-FTIR: 3375, 3309, 3185, 3166, 1622, 1533, 1434, 1400, 1329, 1218 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 1090, 1028, 947, 798, 722 (B<sub>12</sub>F<sub>12</sub><sup>2-</sup>), 663, 629 cm<sup>-1</sup>. These spectroscopic data are identical to those listed for salt **6** in Section 4.3.4.

### Supplementary data

Figures showing the formula units of salts **1-6**, **8**, and **9** as thermal ellipsoid plots. These can be found in a document located at doi:10.1016/J.fluchem.2011.XY.XYZ. Crystallographic data for salts **1-6**, **8**, and **9** have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC **XYZXYZ-XYZXYZ**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk.

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helpful technical discussions, and Mr. Brett A. Wight (AFRL/RZSP) for the  $\text{Cl}^-$  ion chromatography analyses of samples of salt **2**.

**Table 1**

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Metathesis reaction solvent, scale, yield, and melting/decomposition behavior for **1–4** and **6**.<sup>a</sup>

Salt	Solvent	Rxn. scale (g K <sub>2</sub> B <sub>12</sub> F <sub>12</sub> )	Yield	Melting/decomposition behavior
<b>1</b>	CH <sub>3</sub> CN	0.100	90%	Not determined
<b>2</b>	CH <sub>3</sub> CN	0.454	99%	Slowly converted to a dark-brown solid with some liquification and gas evolution up to 398 °C.
<b>2</b>	H <sub>2</sub> O	0.453	84%	Slowly converted to a dark-brown solid with some liquification and gas evolution up to 398 °C.
<b>3</b>	CH <sub>3</sub> CN	0.101	93%	Not determined
<b>4</b>	H <sub>2</sub> O	0.436	90%	Sintered at 190.1–191.2 °C; liquified at 191.3–193.2 °C.
<b>6</b>	H <sub>2</sub> O	0.436	92%	Sintered at 201.3–202.2 °C; liquified at 202.3–204.2 °C.

<sup>a</sup> The five salts listed in this table are as follows: **1**, [1-Et-1-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **2**, [1-H-3-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **3**, [H(imidazolium)]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **4**, [4-NH<sub>2</sub>-1-Me-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **6**, [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]. Drawings of the cations in these salts are shown in Fig. 2.

**Table 2**Crystallographic data and structure refinement parameters for B<sub>12</sub>F<sub>12</sub><sup>2-</sup> salts **1–6**, **8**, and **9**.<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>8</b>	<b>9</b>
Molecular formula	C <sub>12</sub> H <sub>22</sub> B <sub>12</sub> F <sub>12</sub> N <sub>4</sub>	C <sub>8</sub> H <sub>14</sub> B <sub>12</sub> F <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>10</sub> B <sub>12</sub> F <sub>12</sub> N <sub>4</sub>	C <sub>6</sub> H <sub>14</sub> B <sub>12</sub> F <sub>12</sub> N <sub>8</sub>	C <sub>6</sub> H <sub>14</sub> B <sub>12</sub> F <sub>12</sub> N <sub>12</sub>	C <sub>6</sub> H <sub>14</sub> B <sub>12</sub> F <sub>12</sub> N <sub>8</sub>	C <sub>10</sub> H <sub>18</sub> B <sub>12</sub> F <sub>12</sub> N <sub>12</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>16</sub> Ag <sub>2</sub> B <sub>12</sub> F <sub>12</sub> N <sub>16</sub>
Formula weight	580.06	523.95	495.90	555.97	612.01	555.97	606.08	909.83
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Z</i>	4	2	4	2	4	4	4	4
Color of crystal	White	White	White	White	White	White	White	White
Unit cell dims.								
<i>a</i> , Å	15.6537(6)	7.5255(2)	14.245(2)	7.6121(9)	10.882(1)	19.065(2)	25.148(1)	8.9933(5)
<i>b</i> , Å	9.0441(3)	17.0776(4)	14.556(2)	17.941(2)	13.047(1)	9.2222(8)	11.7631(5)	11.7111(6)
<i>c</i> , Å	17.2734(6)	7.9652(2)	10.025(1)	8.494(1)	16.194(2)	14.806(2)	9.0568(4)	28.124(1)
<i>α</i> , deg	90	90	90	90	90	90	90	90
<i>β</i> , deg	90.980(2)	102.234(1)	119.971(9)	113.247(2)	90	120.639(4)	104.634(2)	97.807(2)
<i>γ</i> , deg	90	90	90	90	90	90	90	90
Unit cell vol., Å <sup>3</sup>	2445.1(2)	1000.42(4)	1800.7(5)	1065.9(2)	2299.1(4)	2239.7(4)	2592.2(2)	2934.6(3)
Temperature, K	100(2)	173(2)	100(2)	173(2)	173(2)	173(2)	173(2)	296(2)
Final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.046	<i>R</i> <sub>1</sub> = 0.039	<i>R</i> <sub>1</sub> = 0.086	<i>R</i> <sub>1</sub> = 0.034	<i>R</i> <sub>1</sub> = 0.032	<i>R</i> <sub>1</sub> = 0.069	<i>R</i> <sub>1</sub> = 0.037	<i>R</i> <sub>1</sub> = 0.038
[ <i>I</i> > 2σ( <i>I</i> )]	<i>wR</i> <sub>2</sub> = 0.144	<i>wR</i> <sub>2</sub> = 0.100	<i>wR</i> <sub>2</sub> = 0.217	<i>wR</i> <sub>2</sub> = 0.097	<i>wR</i> <sub>2</sub> = 0.085	<i>wR</i> <sub>2</sub> = 0.196	<i>wR</i> <sub>2</sub> = 0.103	<i>wR</i> <sub>2</sub> = 0.105
GOF on <i>F</i> <sup>2</sup>	1.048	1.124	1.101	1.089	1.069	1.086	1.064	1.030

<sup>a</sup> The eight salts listed in this table are as follows: **1**, [1-Et-1-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **2**, [1-H-3-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **3**, [H(imidazolium)]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **4**, [4-NH<sub>2</sub>-1-Me-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **5**, [4-NH<sub>2</sub>-1-H-1,2,4-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]-4-NH<sub>2</sub>-1,2,4-triazole; **6**, [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]; **8**, [2,6-(NH<sub>2</sub>)<sub>2</sub>-1-H-purinium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]-2H<sub>2</sub>O; **9**, [Ag<sub>4</sub>(1-NH<sub>2</sub>-1,2,3-triazole)<sub>8</sub>][B<sub>12</sub>F<sub>12</sub>]. Drawings of the cations in these salts are shown in Fig. 2.

**Table 3****Distribution A. Approved for public release; distribution unlimited.**

Solid-state parameters for B<sub>12</sub>F<sub>12</sub><sup>2-</sup> and B<sub>12</sub>H<sub>12</sub><sup>2-</sup> salts of heterocyclium(1+) cations.<sup>a</sup>

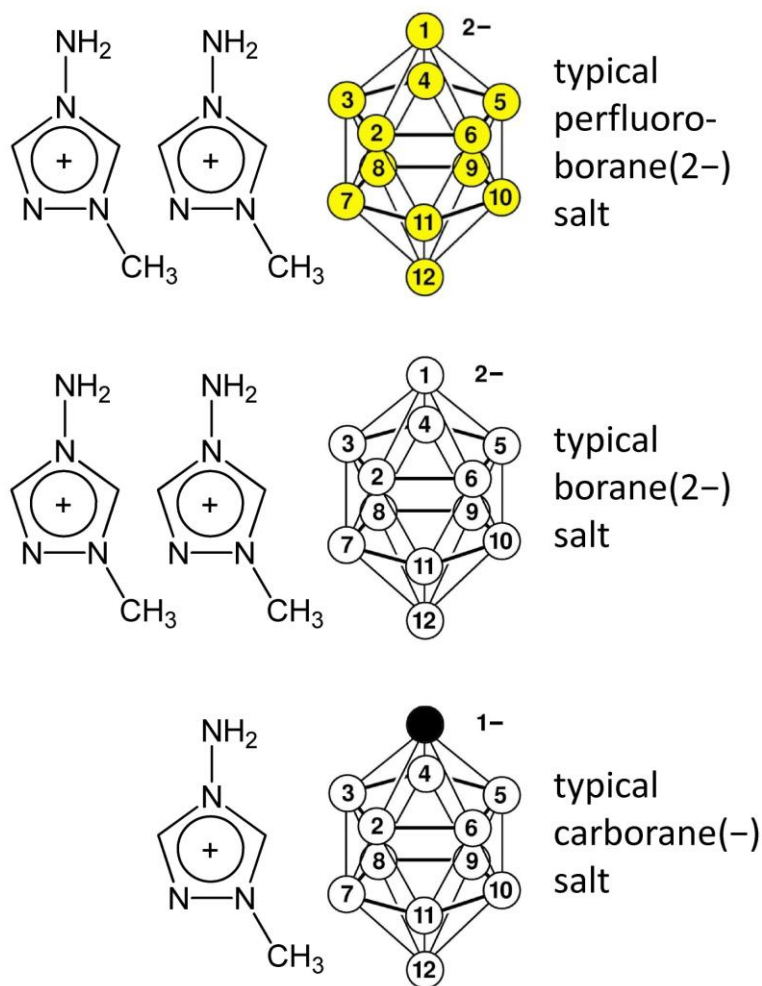
Compound	ref <sup>b</sup>	formula unit vol., Å <sup>3</sup>	density, <sup>c</sup> g cm <sup>-3</sup>	⊖⋯⊖, Å	cation⋯cation, Å <sup>d</sup>
[1-Et-3-Me-imidazolium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] ( <b>1</b> )	tw	611.3(1)	1.576	9.003, 9.044, 10.675	5.708
[1-Et-3-Me-imidazolium] <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ]	[12]	549.4(2)	1.101 <sup>e</sup>	8.268, 8.673, 8.846	4.119
[1-H-3-Me-imidazolium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] ( <b>2</b> )	tw	500.21(2)	1.739	7.525, 7.965, 9.422	4.585
[1-H-3-Me-imidazolium] <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ]	[12]	461.9(4)	1.107 <sup>f</sup>	7.535, 8.167, 9.348	4.113
[H(imidazolium)] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] ( <b>3</b> )	tw	450.2(1)	1.829	7.122, 7.278, 8.938	3.589
[4-NH <sub>2</sub> -1-Me-1,2,4-triazolium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] ( <b>4</b> )	tw	533.0(1)	1.732	7.612, 8.891, 9.925	4.647
[4-NH <sub>2</sub> -1-Me-1,2,4-triazolium] <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ]	[12]	454.3(1)	1.243 <sup>g</sup>	7.036, 8.140, 8.140	4.124
[4-NH <sub>2</sub> -1-H-1,2,4-triazolium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ]-4-NH <sub>2</sub> -1,2,4-triazole ( <b>5</b> )	tw	574.8(1)	1.768	8.100, 8.480, 8.712	5.445 <sup>h</sup>
[1-NH <sub>2</sub> -3-Me-1,2,3-triazolium] <sub>2</sub> [B <sub>12</sub> F <sub>12</sub> ] ( <b>6</b> )	tw	559.9(1)	1.649	7.609, 9.222, 10.692	5.287
[1-NH <sub>2</sub> -3-Me-1,2,3-triazolium] <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ]	[12]	620.1(1)	1.19 <sup>i,j</sup>	8.689, 8.959, 10.324	3.785

<sup>a</sup> See also Table 2. <sup>b</sup> tw = this work. <sup>c</sup> X-ray diffraction-derived densities at 173(2) or 100(2) K. <sup>d</sup> The shortest distance between the centroids of the five-membered rings of the heterocyclium(1+) cations. <sup>e</sup> The density of [1-Et-1-Me-imidazolium][CB<sub>11</sub>H<sub>12</sub>] at 173 K is 1.03 g cm<sup>-3</sup>. <sup>f</sup> The density of [1-H-3-Me-imidazolium][CB<sub>11</sub>H<sub>12</sub>] at 173 K is 1.11 g cm<sup>-3</sup> [12]. <sup>g</sup> The density of [4-NH<sub>2</sub>-1-Me-1,2,4-triazolium][CB<sub>11</sub>H<sub>12</sub>] at 173 K is 1.12 g cm<sup>-3</sup> [12]. <sup>h</sup> This is the shortest distance between cation centroids. The shortest distance between a cation centroid and the five-membered ring centroid of the neutral molecule of 4-NH<sub>2</sub>-1,2,4-triazole is 4.936 Å. <sup>i</sup> The density of [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium][CB<sub>11</sub>H<sub>12</sub>] at 173 K is 1.10 g cm<sup>-3</sup> [12]. <sup>j</sup> The density reported here for [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>] was determined at 25 °C by pycnometry on a vacuum-dried sample because crystals of this compound contained two molecules of CH<sub>3</sub>CN per formula unit [12]. The X-ray density of [1-NH<sub>2</sub>-3-Me-1,2,3-triazolium]<sub>2</sub>[B<sub>12</sub>H<sub>12</sub>]-2CH<sub>2</sub>CN is 1.132 g cm<sup>-3</sup> [12].

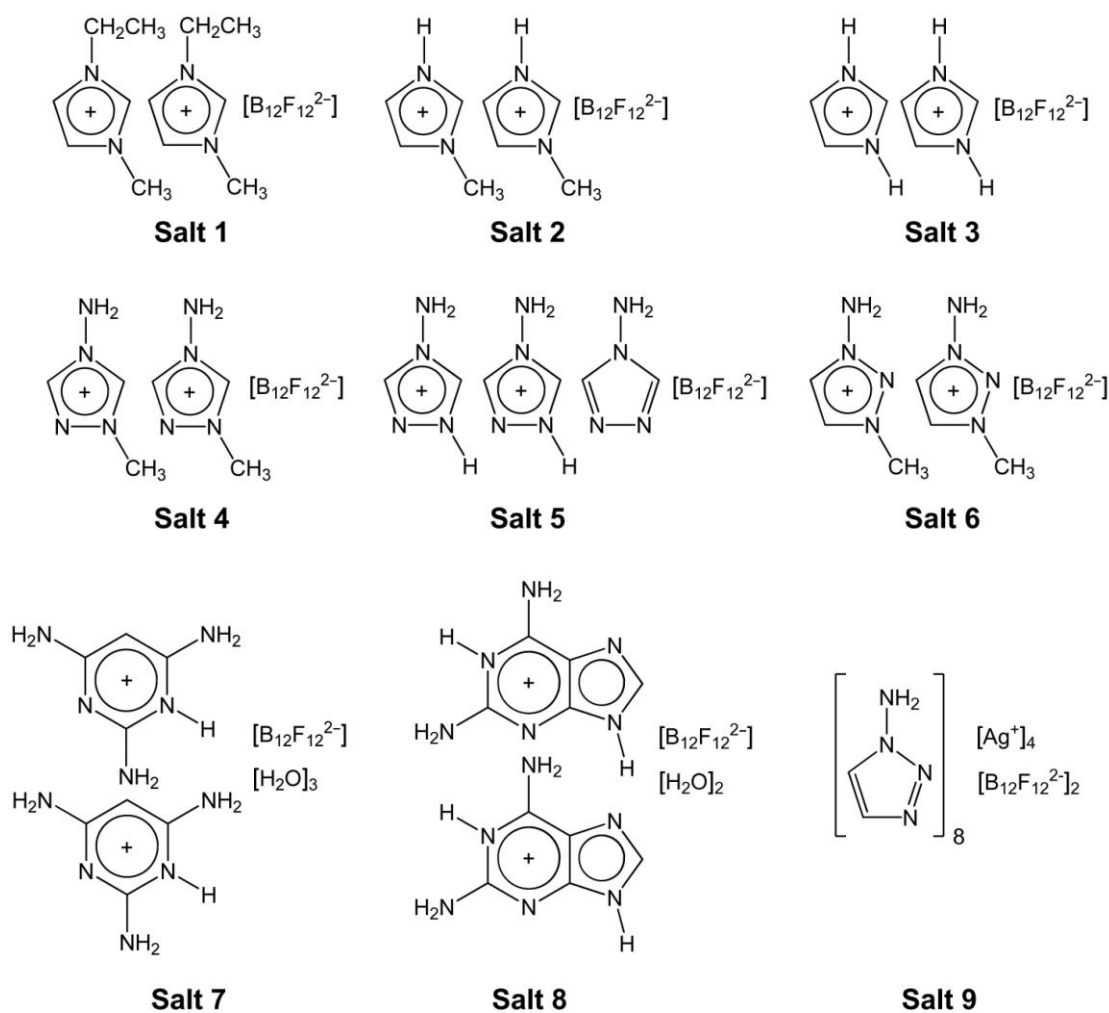
**Table 4**Structural results for tetrameric silver(I) triazole compounds.<sup>a</sup>

parameter	[Ag <sub>4</sub> (tz-1) <sub>8</sub> ][B <sub>12</sub> F <sub>12</sub> ] <sub>2</sub>	[Ag <sub>4</sub> (tz-2) <sub>7</sub> ][ClO <sub>4</sub> ] <sub>4</sub>	[Ag <sub>4</sub> (tz-3) <sub>6</sub> ][NO <sub>3</sub> ] <sub>4</sub> ·4H <sub>2</sub> O
reference	this work	[20]	[21]
Ag1–N	2.211(3), 2.238(3), 2.322(4) Å	2.179(4), 2.200(4), 2.314(5) Å	2.230(3), 2.247(3), 2.317(3)
Ag1–F	2.960(3) Å		
Ag2–N	2.255(3), 2.263(3), 2.404(3), 2.492(4) Å	2.283(4), 2.283(4), 2.326(5), 2.369(4)	2.253(3), 2.255(3), 2.311(3) Å
Ag2–F	2.806(3) Å		
Ag1 bond- valence sum	1.05	1.09	0.98
Ag2 bond- valence sum	1.13	1.14	0.96
Ag1⋯Ag2	3.764(2) Å	3.156(1) Å	3.714(2) Å
Ag1⋯Ag2'	3.858(2) Å	3.632(1) Å	3.905(2) Å
Ag2⋯Ag1⋯Ag2	114.2(1)°	156.41°(3)	92.8(1)°
Ag1⋯Ag2⋯Ag1	65.8(1)°	132.68°(3)	87.2(1)°

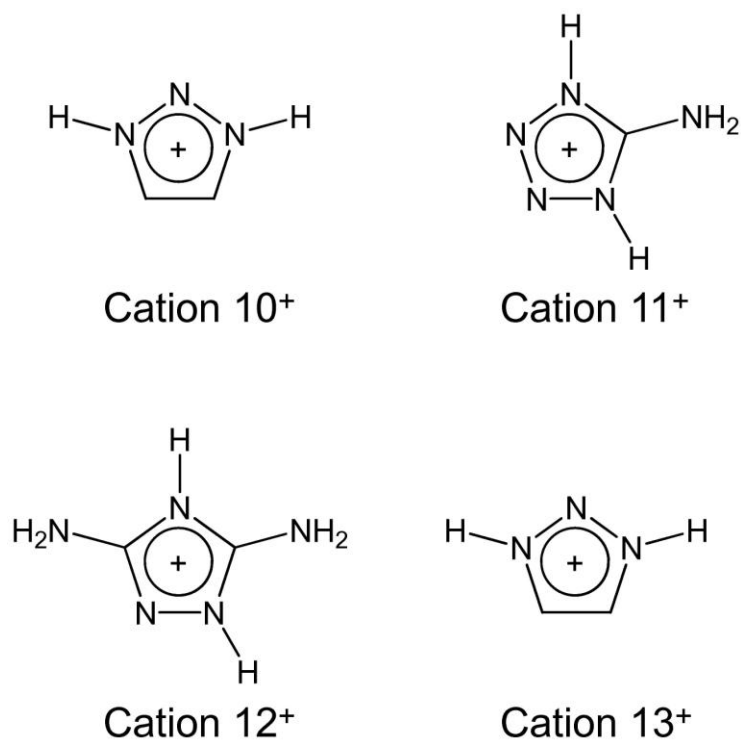
<sup>a</sup> tz-1 = 1-NH<sub>2</sub>-1,2,3-triazole; tz-2 = 4-NH<sub>2</sub>-1,2,4-triazole; tz-3 = 4-(3-C<sub>6</sub>H<sub>4</sub>OH)-1,2,4-triaz



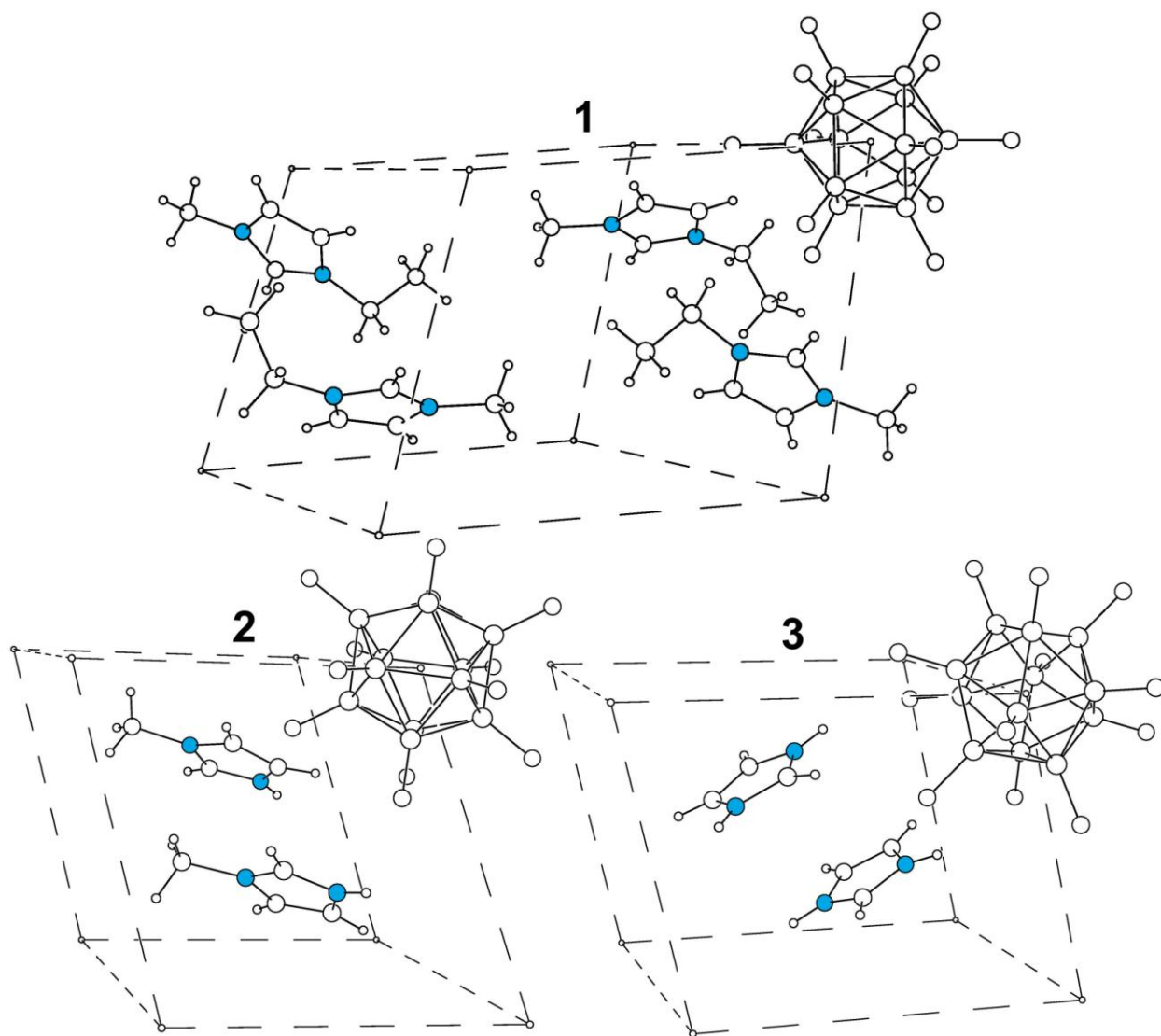
**Fig. 1.** Examples of binary heterocyclium(1+) salts of  $B_{12}F_{12}^{2-}$  (top),  $B_{12}H_{12}^{2-}$  (middle), and  $CB_{11}H_{12}^{-}$  (bottom). Each vertex of the icosahedral anions bears an F atom (top) or a H atom (middle and bottom). The black sphere in the drawing of the  $CB_{11}H_{12}^{-}$  anion is the C-H vertex. The anion drawings also show the numbering of the vertexes.



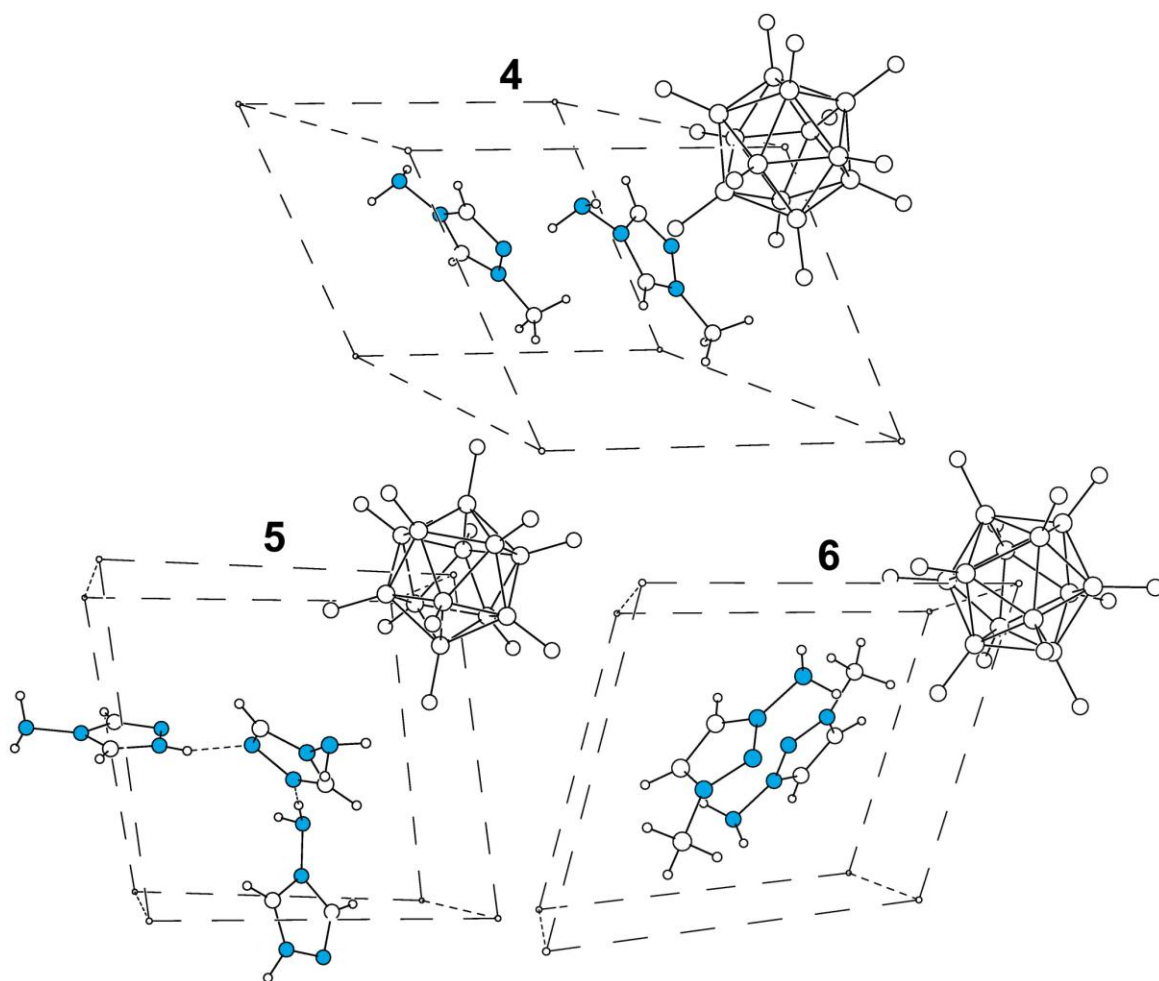
**Fig. 2.** The compositions of salts **1–9** studied in this work. The positive charge in salt **8** is delocalized over the entire fused-ring system. The positive charges in salt **9** are delocalized to some extent over the eight triazole molecules, which are coordinated to the  $\text{Ag}^+$  cations.



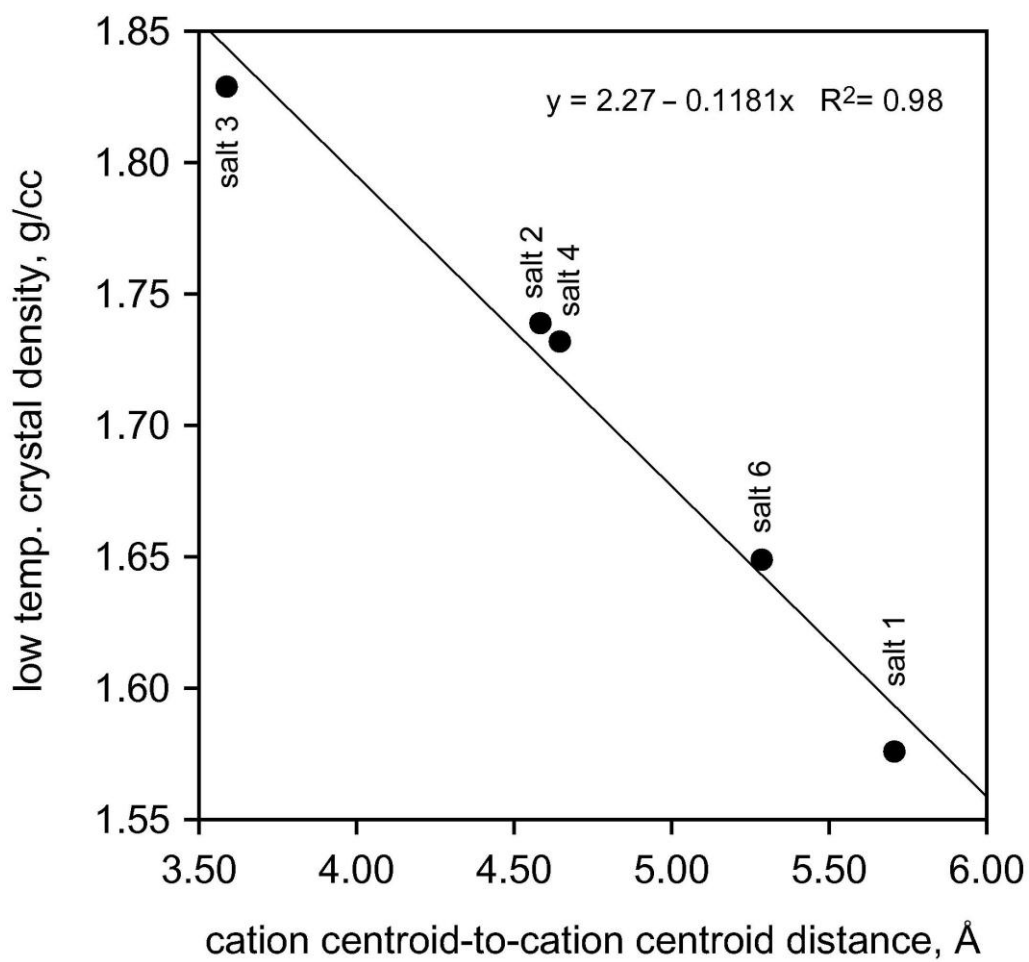
**Fig. 3.** Heterocyclium(1<sup>+</sup>) cations that did not readily form binary [heterocyclium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] salts using the metathesis reactions shown in Scheme 1.



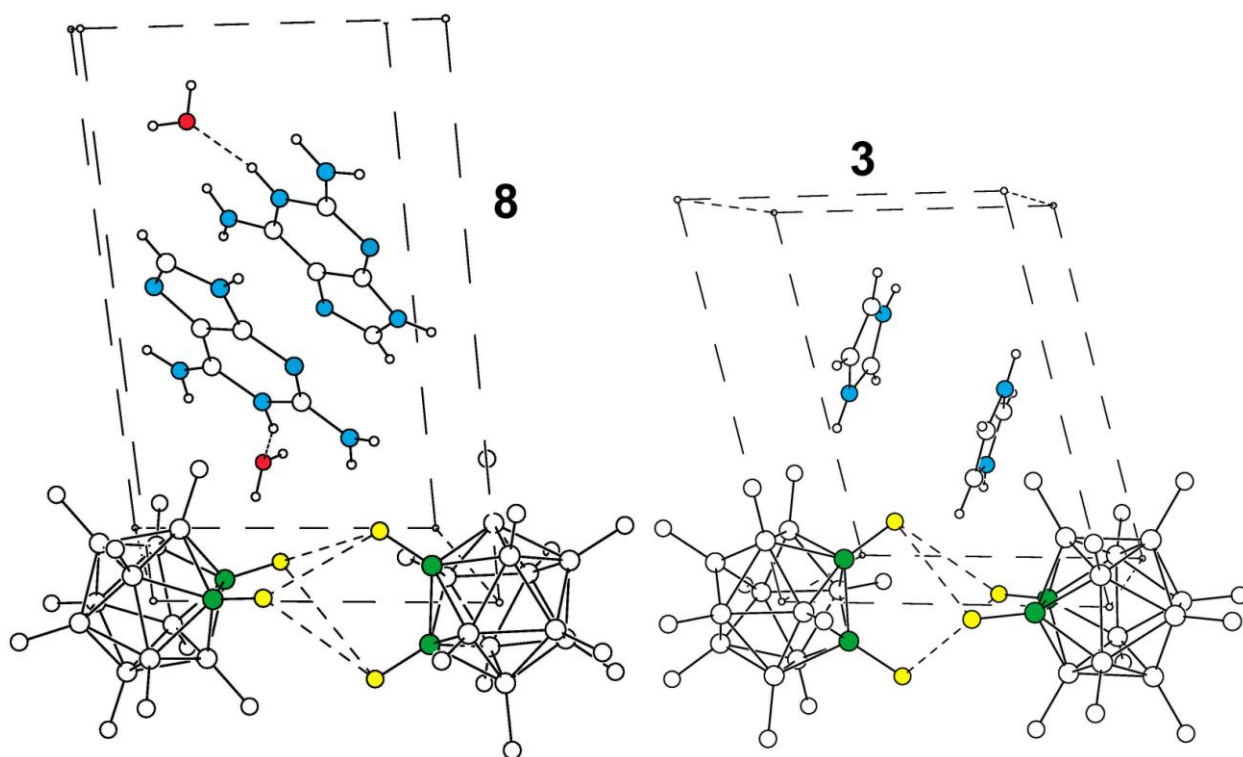
**Fig. 4.** The packing of pairs of heterocyclium(1<sup>+</sup>) cations inside rhombs of eight  $B_{12}F_{12}^{2-}$  anions in the structures of [1-Et-1-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**1**, top), [1-H-3-Me-imidazolium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**2**, bottom left), and [H(imidazolium)]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**3**, bottom right). The blue spheres are N atoms. The eight corners of the rhombs are composed of B<sub>12</sub> centroids. Each rhomb contains two complete cations or, in the case of **1**, parts of four cations that yield two complete cations. Structural drawings of these cations in salts **1-3** are seen in Fig. 2.



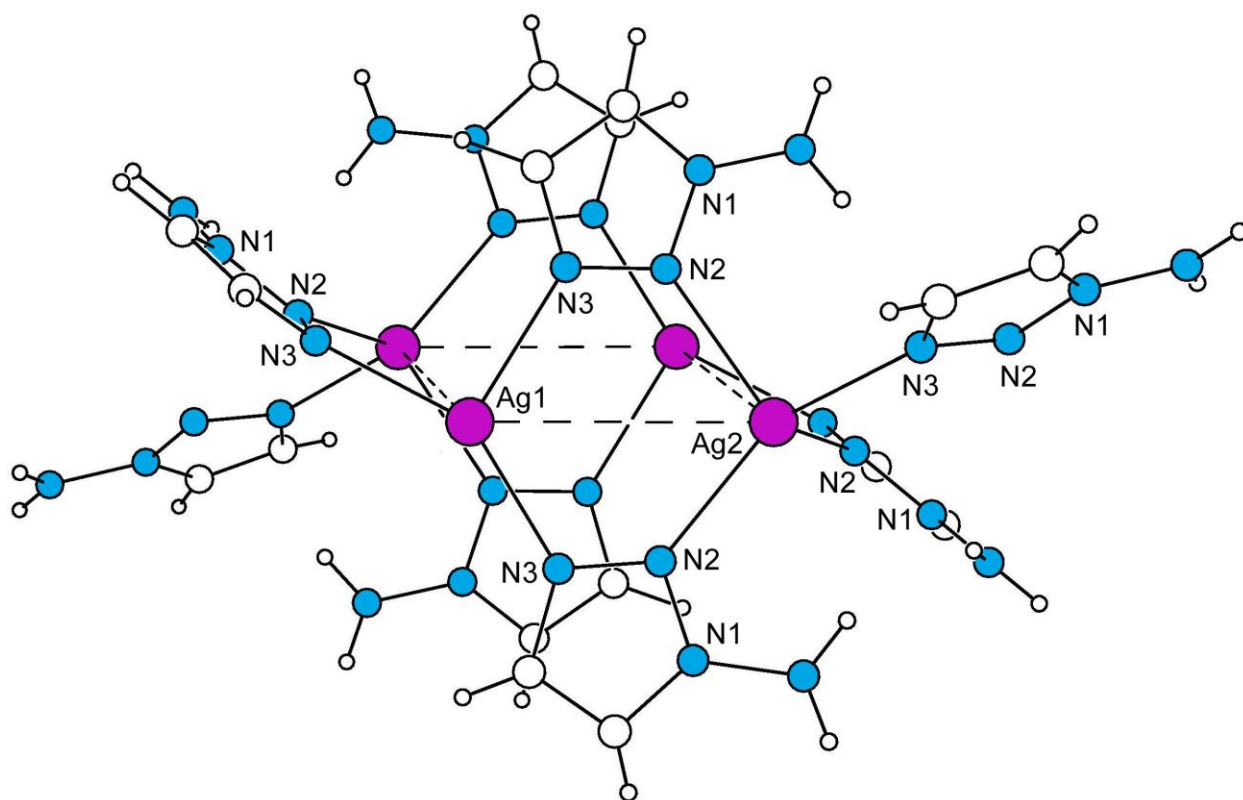
**Fig. 5.** The packing of pairs of heterocyclium(1+) cations inside rhombs of eight  $\text{B}_{12}\text{F}_{12}^{2-}$  anions in the structures of  $[\text{4-NH}_2\text{-1-Me-1,2,4-triazolium}]_2[\text{B}_{12}\text{F}_{12}]$  (**4**, top),  $[\text{4-NH}_2\text{-1-H-1,2,4-triazolium}]_2[\text{B}_{12}\text{F}_{12}]\cdot\text{4-NH}_2\text{-1,2,4-triazole}$  (**5**, middle), and  $[\text{1-NH}_2\text{-3-Me-1,2,3-triazolium}]_2[\text{B}_{12}\text{F}_{12}]$  (**6**, bottom). The blue spheres are N atoms. The eight corners of the rhombs are composed of  $\text{B}_{12}$  centroids. Each rhomb contains two complete cations in **4** and **6**. In **5**, each rhomb contains parts of four triazolium cations and two triazole molecules that yield two complete cations and one complete triazole molecule (each five-membered ring is nearly centered on each of the six faces of the anion rhomb). Structural drawings of these cations in salts **4-6** are seen in Fig. 2.



**Fig. 6.** Plot of salt density and the shortest cat···cat distance for the five  $B_{12}F_{12}^{2-}$  salts **1–4** and **6**. The line is a linear least-squares fit to the five points.



**Fig. 7.** The packing of 2,6-(NH<sub>2</sub>)<sub>2</sub>-1-H-purinium(1+) cations and H<sub>2</sub>O molecules inside the rhomb of eight B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions in the structure of [2,6-(NH<sub>2</sub>)<sub>2</sub>-1-H-purinium]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>]·2H<sub>2</sub>O (**8**) and the packing of H(imidazolium)(1+) cations inside the rhomb of B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions in the structure of [H(imidazolium)]<sub>2</sub>[B<sub>12</sub>F<sub>12</sub>] (**3**) (the corners of the rhombs are composed of B<sub>12</sub> centroids). The blue, red, green, and yellow spheres are N, O, B, and F atoms, respectively. These drawings emphasize the dovetail-like packing of the B<sub>12</sub>F<sub>12</sub><sup>2-</sup> anions. The ⊙⋯⊙ distances for the two anions shown are 7.423 Å for **8** and 7.122 Å for **3**. The angles between the two highlighted F–B–B–F planes in each drawing are 78.7° for **8** and 90° for **3**. The F⋯F distances shown are 2.779, 3.193, 3.689, and 3.796 Å in **8** and 2.908 (× 2) and 3.108 Å (× 2) in **3**. Structural drawings of these cations in salts **3** and **8** are seen in Fig. 2.



**Fig. 8.** The centrosymmetric  $\text{Ag}_4(1\text{-NH}_2\text{-}1,2,3\text{-triazole})_8^{4+}$  tetracation in the structure of  $[\text{Ag}_4(1\text{-NH}_2\text{-}1,2,3\text{-triazole})_8][\text{B}_{12}\text{F}_{12}]$  (**9**). The blue and purple atoms are N atoms and  $\text{Ag}^+$  cations, respectively. The four  $\text{Ag}^+$  ions are rigorously coplanar with  $\text{Ag}\cdots\text{Ag}$  distances of 3.764(2) and 3.858(2) Å and  $\text{Ag}\cdots\text{Ag}\cdots\text{Ag}$  angles of 65.8(1) and 114.2(1)°.

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### Graphical Abstract

Pairing heterocyclic cations with *closo*-dodecafluorododecaborate( $2^-$ ). Synthesis of binary heterocyclium( $1^+$ ) salts and a  $\text{Ag}_4(\text{heterocycle})_8^{4+}$  salt of  $\text{B}_{12}\text{F}_{12}^{2-}$

John L. Belletire<sup>a</sup>, Stefan Schneider<sup>b</sup>, Scott A. Shackelford<sup>b</sup>, Dmitry V. Peryshkov<sup>c</sup>, Steven H. Strauss<sup>c</sup>

<sup>a</sup>ERC, Inc., AFRL/RZSP, Edwards AFB, CA 93524-7680, USA

<sup>b</sup>Air Force Research Laboratory, AFRL/RZSP, Edwards AFB, CA 93524-7680, USA

<sup>c</sup>Department of Chemistry, Colorado State University, Ft. Collins, CO 80523, USA

